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7110

MEMO-letter

DEPARTMENT OF ENVIRONMENTAL SERVICES

P.O. Box 95 - 6 Hazen Drive
Concord, New Hampshire 03301-6528
(603) 271-3503

Given: <u>SAVAGE WELLS</u>
Breast: <u>3/2/88</u>
Other: _____

TO DIANA LETTRO RPM
USEPA-WASTE MGMT DIV
JFK FEDERAL BLDG
BOSTON MA 02203

Date 8/4/88

Subject STATE OVERSIGHT POP

Diana,

Please find attached the NHDES-
WMD's revised Project Operations
Plan for field oversight of field
activities at the Savage Municipal Well
Site in Milford, NH.

Dick P.

412 14-0000

71

Site:	WEE (111)
Break:	5/1/5
Other:	

State Oversight Support
of
Field Investigations
for the
Remedial Investigation/Feasibility Study
at the
Savage Municipal Well Hazardous Waste Site

5/1/5

Project Operations Plan

PROJECT OPERATIONS PLAN

- I. INTRODUCTION
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I. INTRODUCTION

I. INTRODUCTION

The following Project Operations Plan describes the tasks to be conducted by New Hampshire Department of Environmental Services personnel under the State/EPA Cooperative Agreement for the State oversight of Potentially Responsible Party field investigations. The States primary role in oversight support will be to ensure compliance to the intent of the Administrative consent Order and its attached Work Plan and ensure quality control of field procedures and/or field sampling.

The Project Operations Plan is a compilation of four site specific plans that are used to implement the Remedial Investigation/Feasibility Study as set forth in the Administrative Consent Order. The four plans are the Site Management Plan, Sampling and Analysis Plan, the Quality Assurance Project Plan, and the Health and Safety Plan.

The Site Management Plan will provide a written understanding of how various aspects of all activities funded under the State/EPA Cooperative Agreement will be managed.

The Sampling and Analysis Plan defines the level of effort of the State's split/confirmatory sampling program to ensure quality data is gathered during the Remedial Investigation/Feasibility Study.

The Quality Assurance Project Plan defines procedures used in the State's oversight effort to ensure data of the highest quality is produced to provide comparability to the Potentially Responsible Parties contractor's data.

The Health and Safety Plan provides guidelines for the protection of State personnel during oversight activities at the Savage Municipal Well Site.

Whenever appropriate the contractor's Project Operation Plan is referenced in order to ensure compatibility of the States oversight efforts to the contractor's level of effort in conducting field activities. Accordingly, it may be necessary to modify the scope of the States oversight activities if the Potentially Responsible Parties contractor's level of effort is modified during the conductance of the Remedial Investigation/Feasibility Study.

II. BACKGROUND

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A. Site Location and History

The Savage Municipal Wellfield site encompasses 0.6 square miles and is located in southwestern New Hampshire in the Town of Milford in Hillsborough County (see Figures 1 and 2). The study area includes four major industrial facilities and two high-yield industrial process water supply wells. The Savage Well, a municipal water supply well formerly used by the Town of Milford, is located approximately 2 miles west of the center of Milford. The land use in the area includes agriculture and heavy industry, interspersed with commercial and residential development.

The site lies within the USGS Milford 7-1/2-minute quadrangle and is approximately located at 42°50'30" north latitude and 71°40' west longitude. The Savage Well site is situated on a broad flat flood plain of the Souhegan River. To the north and south are rolling and hilly uplands which rise from 100 to 300 feet above the flood plain.

The Savage Well is a gravel packed well with a sustained yield of approximately 500 gallons per minute. The Town of Milford utilized this well for municipal water supply purposes from 1960 to 1983, during which time the well was pumped for six to seven hours per day for a total yield of approximately 210,000 gpd.

During routine water quality monitoring by the State of New Hampshire, concentrations above proposed Maximum Contaminant Levels (MCL's) of several volatile organics were detected in the Savage Well and a water supply well used by a mobile home park located west of the Savage Well. Analysis of the Savage Well samples indicated that tetrachloroethylene, 1,1,1-trichloroethane, 1,2-trans-dichloroethylene, 1,1-dichloroethane, and trichloroethylene were present. The mobile home park supply well within the site area contained the same organic contaminants with the exception of 1,1-dichloroethane. Both wells were discontinued as public water supplies in February of 1983.

The Town of Milford relied on other existing water supplies until an alternate supply was developed in the summer of 1983. The mobile home park was connected to the municipal system using emergency funding available through the EPA. Several high yield wells near the Savage Well continue to utilize local groundwater for industrial process and cooling waters.

Further sampling of surface water and groundwater by New Hampshire Water Supply and Pollution Control Division (NHWSPCD) indicated that contamination was widespread throughout the region. NHWSPCD in conjunction with the New Hampshire Division of Public Health Services (DPHS) initiated investigations into the potential sources of the contaminants. An inspection of the two major industrial facilities in the area and of several of the smaller commercial establishments was conducted to assess the prevailing waste management practices and the potential impacts of these on groundwater quality. Subsequently, hydrogeologic investigations were initiated by two of the local industrial entities within the facility boundaries.

The work performed by NHWSPCD is complete at this time and a final report with its findings has been released. Work being performed by the local industries is continuing.

The Savage Municipal Well site ranks 430 on the National Priorities List (NPL) of sites eligible for funding under the Comprehensive Environmental, Response, Compensation and Liability Act of 1980 (CERCLA), more commonly known as Superfund.

B. Enforcement and Settlement

On June 18, 1985, USEPA issued a notice to four companies considered potentially responsible parties (PRP's) for the contamination in the vicinity of the Savage Municipal Well Site in Milford, New Hampshire. The notice sent to Hitchiner Manufacturing Company, Inc., Hendrix Wire and Cable Corporation, New England Steel Fabricators, Inc., and the O.K. Tool Company informed the companies of their potential liability for the cleanup costs at this site under CERCLA and offered the opportunity to undertake voluntary cleanup activities.

On January 13, 1987 the USEPA sent a formal offer to the PRP's to conduct a Remedial Investigation/Feasibility Study. The objectives of the Remedial Investigation are to evaluate existing information, identify data gaps, and perform the necessary field work and laboratory analyses to define the extent of contamination and the potential public health risks related to the Savage Municipal Well site. Furthermore, it is necessary to distinguish between potential sources and to identify the interrelationships between sources. After defining the nature and extent of contamination, the need for remedial action can be defined. Remedial action alternatives will be evaluated. This will lead to the development of a selected remedial action alternative during the Feasibility Study.

The objectives of the Feasibility Study are to evaluate the need for the remedial actions, establish response criteria and objectives, identify the remedial action alternatives, evaluate the alternatives, recommend a cost-effective alternative that provides adequate protection of public health and welfare and the environment, and prepare a conceptual design for the selected remedial action. The FS will focus on the development and evaluation of measures to be taken to alleviate all identified contamination problems.

On August 10, 1987 an Administrative Order by Consent was finalized in which the Potentially Responsible Parties agreed with the USEPA to conduct the RI/FS according to an attached workplan and any amendments agreed to by the USEPA. This RI/FS work plan has been developed to address the needs of EPA, the appropriate state agencies, and the public within the surrounding area who are directly affected by both the contamination problem and any proposed remedial actions. On September 24, 1987 HMM Associates was contracted to conduct the RI/FS on behalf of the PRP's.

On October 29, 1987 the Governor and Executive Council of the State of New Hampshire approved acceptance of funds in a Cooperative Agreement with the USEPA to provide for State Oversight of Field Activities associated with the RI/FS process.

III. SITE MANAGEMENT PLAN

SITE MANAGEMENT PLAN

The objectives of the Site Management Plan (SMP) is to provide the EPA with a written understanding and commitment of how various aspects of all activities funded under the Cooperative Agreement will be managed.

The Project Operations Plan is a compilation of four site specific plans that are used to implement the Remedial Investigation/Feasibility Study as set forth in the Administrative Consent Order. The four plans are the Site Management Plan, Sampling and Analysis Plan, the Quality Assurance Project Plan, and the Health and Safety Plan.

The Site Management Plan will provide a written understanding of how various aspects of all activities funded under the State/EPA Cooperative Agreement will be managed.

The Sampling and Analysis Plan defines the level of effort of the State's split/confirmatory sampling program to ensure quality data is gathered during the Remedial Investigation/Feasibility Study.

The Quality Assurance Project Plan defines procedures used in the State's oversight effort to ensure data of the highest quality is produced to provide comparability to the Potentially Responsible Parties contractor's data.

The Health and Safety Plan provides guidelines for the protection of State personnel during oversight activities at the Savage Municipal Well Site.

Whenever appropriate the contractor's Project Operation Plan is referenced in order to ensure compatibility of the State's oversight efforts to the contractor's level of effort in conducting field activities. Accordingly, it may be necessary to modify the scope of the State's oversight activities if the Potentially Responsible Parties contractor's level of effort is modified during the conductance of the Remedial Investigation/Feasibility Study.

All activities will be consistent with the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) as amended by the Superfund Amendments and Reauthorization Act of 1986 (SARA) and the National Contingency Plan 40 CFR 300.

Specific objectives and provisions of the SMP include but are not limited to the following:

Task IV Coordination

- 1) Attendance of meetings, briefings and technical sessions to provide oversight support
- 2) Submittal of quarterly progress reports with a budget summary. Reports will include a brief discussion of progress problems resolved, anticipated problems, recommended solutions, deliverables submitted, upcoming planned activities, key personnel changes, travel, percent complete and schedule.

Table I shows the level of effort projected for each subtask by all personnel involved in the State oversight of field investigations at the Savage Municipal Well Hazardous Waste Site.

Project Scope of Work and Budget will require close monitoring due to the nature of the oversight work as additional work items not previously envisioned may become necessary during such assignments. The work to be accomplished and budget expanded for such items outside that specified in the Oversight Work Plan and/or the Consent Order will be indentified to EPA for approval.

A brief biographical sketch of key personnel funded under the States oversight cooperative agreement follows, with a description of their duties and responsibilities.

TABLE I Manhours vs. Task

Task		Chief Engineer (Hours)	Administrator (Hours)	On-Scene Coordinator (Hours)	Hydrogeologist (Hours)	Environmentalist (Hours)	Accountant (Hours)	Clerk Typist (Hours)
Task I Background Information Review		(17.0)	(38.0)	(97.5)	(13.5)	(14.5)	(75.0)	(75.0)
1	EPA Consent Order and Work Plan	1.0	4.0	15.0	4.0	7.5		15.0
2	State/EPA Cooperative Agreement	7.5	15.0	37.5	3.5	1.0	75.0	30.0
3	Site Project Operations Plan	7.5	15.0	15.0	3.0	3.0		15.0
4	Other reports and/or information	1.0	4.0	30.0	3.0	3.0		15.0
Task II Oversight of Field Work (Office)								
1	Preparation of State Project Operations Plan	(16.5)	(30.0)	(90.0)	(12.0)	(30.0)		(75.0)
a	Site Management Plan	7.5	15.0	45.0	3.0	3.0		15.0
b	Sampling and Analysis Plan	3.0	5.0	15.0	3.0	3.0		15.0
c	Quality Assurance Project Plan	3.0	5.0	15.0	3.0	7.5		30.0
d	Health and Safety Plan	3.0	5.0	15.0	3.0	7.5		15.0
2	Evaluation and Comment on Procedures	(20.0)	(75.0)	(112.0)	(46.5)	(135.0)		(150.0)
a	Geophysical surveys	4.0	15.0	22.5	15.0			30.0
b	Air sampling	4.0	15.0	22.5	3.0			30.0
c	Surface water and sediment sampling	4.0	15.0	22.5	3.0	45.0		30.0
d	Monitoring well installation	4.0	15.0	30.0	18.0			30.0
e	Groundwater sampling	4.0	15.0	15.0	7.5	90.0		30.0
3	Bi-weekly Reporting	(12.0)	(24.0)	(90.0)	(48.0)	(48.0)		(150.0)
Task III Oversight of Field Work (Field)								
1	Observe and document field work	(38.0)	(90.0)	(350.0)	(360.0)	(220.0)		(210.0)
a	Geophysical surveys	2.0	15.0	37.5	37.5	15.0		15.0
b	Air Sampling	2.0	10.0	45.0	7.5	30.0		15.0
c	Surface water and sediment sampling	2.0	10.0	45.0		73.0		30.0
d	Monitoring well installation	30.0	30.0	172.5	300.0	15.0		75.0
e	Groundwater sampling	2.0	25.0	50.0	15.0	87.0		75.0
2	Collect Split Samples					(50.0)		
3	Maintain Photographic Records			(3.0)	(7.5)	(2.5)		
Task IV Coordination		(46.5)	(93.0)	(127.5)	(12.5)		(365.0)	(140.0)
1	Attendance of meetings	22.5	37.0	37.5	12.5			15.0
2	Quarterly Progress Reports	24.0	56.0	90.0				125.0
TOTAL HOURS		150.0	350.0	870.0	500.0	500.0	440.0	4800.0

(4) - TOTAL HOURS PER TASK

BIOGRAPHICAL SKETCH

Michael A. Sills, Ph.D., P.E.
Chief Engineer

Dr. Sills holds a B.S. in Mechanical Engineering from Worcester Polytechnical Institute, an M.S. in Civil Engineering (Sanitary) from the University of Connecticut and a Ph.D. in Environmental Engineering and Science from the University of Connecticut. He is also a registered Professional Engineer, a member of AWWA, WPCF, ASCE, ASTSWAMO, NEWMOA, and the NEIWPEC. Dr. Sills is currently Chief Engineer of the Waste Management Division, Department of Environmental Services (DES). In addition, he formerly held the positions of Director of the Groundwater Protection Bureau and Administrator of the Superfund Site Management Bureau of DES. Dr. Sills has worked in the consulting engineering field and manufacturing of pollution abatement and life support systems in the space program. He has published numerous articles on environmental engineering, groundwater protection, hazardous waste management and subsurface contamination topics.

The Chief Engineer is responsible formulating the Waste Management Division's engineering program objectives. The Chief Engineer will make the administrative and technical decisions required for the development and implementation of the States oversight agreement, and will attend meetings to make important contact between consultant engineers, town, state and federal officials as well as the public.

BIOGRAPHICAL SKETCH

Carl W. Baxter, P.E.
Administrator

Mr. Baxter holds a B.S. in Civil Engineering from the University of Maine and an M.S. in Civil Environmental Engineering from the University of Massachusetts. He is a registered Professional Engineer and a member of several societies. Currently, Mr. Baxter is the Administrator of the Superfund Site Management Bureau in the Waste Management Division of the New Hampshire Department of Environmental Services. This Bureau is responsible for administering the Federal Superfund (CERCLA/SARA) program in New Hampshire. Mr. Baxter has worked over 10 years in both government and consulting engineering, doing municipal and industrial water and wastewater engineering and hazardous waste engineering.

The Administrator is responsible for supervising the engineering activities associated with the Waste Management Division's Superfund Site Management Bureau. The Administrator coordinates activities with other divisions within the State i.e. Laboratory Services, Administrative Services, Air Resources, Water Resources, Water Supply and Pollution Control, Office of State Planning, and the Attorney General's Office. Important contacts are made by the Administrator to insure successful implementation of the project, such as securing permits easements and clearances.

BIOGRAPHICAL SKETCH

Richard Pease, P.E.
On-Scene Coordinator

Mr. Pease holds a B.S. in Civil Engineering, Environmental Option from the University of New Hampshire. He is also a registered Professional Engineer in the State of New Hampshire. Currently Mr. Pease is a remedial project manager for the Superfund Site Management Bureau of the Waste Management Division, New Hampshire Department of Environmental Services. As a project manager he is responsible for administering remedial activities at several Superfund sites in New Hampshire.

The On-Scene Coordinator (OSC) is responsible for directing the State's oversight of the PRP's field investigation program and providing a daily on site presence to insure compliance with workplan activities and timetables. The OSC will be required to organize the personnel necessary to effect an efficient oversight service. Appropriate personnel will be scheduled and signed specific oversight tasks. The OSC in addition to observing, evaluating, and documenting all aspects of field activities, the OSC will insure that the Hydrogeologist III and the Environmentalist II comply with the intent of the Work Plan and the Project Operations Plan in their assigned areas of responsibility.

Preparation of all reports i.e. State Oversight Project Operations Plan, Comments and recommendations to the Site Project Operations Plan, bi-weekly progress reports and quarterly project reports will be the responsibility of the On-Scene Coordinator. The OSC will be the main point of contact within the state for all communications and will attend all meetings relative to the conductance of the States Oversight Project Operations Plan.

BIOGRAPHICAL SKETCH

Michael J. Robinette, P.G.
Hydrogeologist III

Mr. Robinette holds a B.A. in Geology from the University of New Hampshire and an M.S. in Hydrology from the University of Idaho. He is also a registered Professional Geologist in the state of Idaho. Currently Mr. Robinette is a remedial project manager and chief hydrogeologist in the Waste Management Division of the New Hampshire Department of Environmental Services. As a project manager he is responsible for administering several Superfund sites in the state. As staff hydrogeologist he is responsible for hydrogeologic review and oversight of state and federal funded uncontrolled hazardous waste sites.

The Hydrogeologist III is responsible for providing the technical expertise required to evaluate the geophysical and hydrogeological investigations. Duties will include overseeing the geophysical surveys, the monitoring well installation program, and aquifer testing procedures. The Hydrogeologist III reports directly to the On-Scene Coordinator.

BIOGRAPHICAL SKETCH

Boyd P. Smith, B.S.
Environmentalist II

Mr. Smith currently holds a Bachelor of Science in Geology with a minor in Hydrology from the University of New Hampshire (UNH) in Durham, New Hampshire. He is continuing his education at UNH as a candidate for a Master of Science in Hydrology. The focus of his work is in the area of hydrogeology, with special emphasis on groundwater flow in bedrock aquifers.

Mr. Smith has been employed by the State of New Hampshire for three years and works in the Superfund Management Bureau of the Waste Management Division. He has been responsible for collection of field data, and manages the water quality sampling programs of several Superfund sites. He has had training in personal safety on hazardous waste sites, and has attended numerous programs in the area of groundwater monitoring.

The Environmentalist II will observe and document all aspects of the environmental sampling and analysis program and take split/confirmatory samples as described in the Sampling and Analysis Plan. In addition, the Environmentalist II will assemble data and the required QA/QC reports. The Environmentalist II will report directly to the On-Scene Coordinator.

The Accountant II is responsible for establishing and maintaining controls and records consistent with state and federal requirements accounting functions will be performed in the legally applicable manner for cost recovery. The Accountant II will prepare periodic budgetary reports and statements, and perform analysis required to monitor expenditure status.

The Clerk Typist will perform secretarial duties such as setting up and typing tabulated statistical studies, correspondence, reports, and any forms relating to technical or administrative matters.

Table I shows the level of effort projected for each subtask by all personnel involved in the State oversight of field investigations at the Savage Municipal Well Hazardous Waste Site.

IV. SAMPLING AND ANALYSIS PLAN

SAMPLING AND ANALYSIS PLAN

A representative number of split/confirmatory samples will be collected by the state for each sampling episode conducted by the Contractor. The purpose of this effort is to provide quality data that may be used to determine quantitative comparability and compatibility with the Contractor's sampling data and help in assessing its validity.

The Contractor should notify the On-Scene Coordinator four weeks prior to the sampling episode or as soon as possible, to allow for split sampling to be scheduled. At the request of the State, the Contractor will be required to provide parallel samples in containers using identical sampling procedures as used when collecting the PRP's samples. Collection methods are to be described in the Contractors Sampling and Analysis Plan. Laboratory analytical procedures are described in the States Quality Assurance Project Plan.

The State/EPA Cooperative Agreement provides funds to take samples for volatile organic chemical analysis and HSL analysis. Table I below shows the anticipated number of samples to be taken projected from Table 2 of the Work Plan - Multi-Media Field Investigation. These numbers reflect a minimum of 35 well clusters with two wells at each cluster. The actual number of individual wells at a well cluster will be dependent upon properties of the overburden materials encountered.

All sampling locations should be chosen with EPA's concurrence. Should EPA not be in the field when a sampling location is chosen, it will be the responsibility of the OSC to approve the selection of the location and to notify EPA's Project Coordinator as soon as possible.

TABLE I

<u>Sample Episode</u>	<u>Total Samples*</u>	<u>Split Samples*</u>
Existing Monitoring Wells (approx.)	40	4
Proposed Monitoring Wells	74	7
Follow-up #I	15	2
#II	15	2
#III	15	2
#IV	15	2
Surface Waters	<u>21</u>	<u>2</u>
Total Aqueous	195	21
Sediment	17	2
Air (Phase II)	5	1

*Anticipated number subject change with EPA's written concurrence

V. HEALTH AND SAFETY PLAN

SAVAGE MUNICIPAL WELL SITE SAFETY PLAN

SITE SAFETY PLAN FOR SITE INVESTIGATIONS CARRIED OUT UNDER THE COMPREHENSIVE ENVIRONMENTAL RESPONSE, COMPENSATION AND LIABILITY ACT (CERCLA) AS AMENDED BY THE SUPERFUND AMENDMENTS AND REAUTHORIZATION ACT (SARA)

NEW HAMPSHIRE DEPARTMENT OF ENVIRONMENTAL SERVICES

GENERAL

The purpose of this plan is to assign responsibilities, establish personal protection standards and mandatory operating procedures, and provide for contingencies that may arise while operations are being conducted at the Savage Municipal Well site. All state personnel at this site will be required to follow this safety plan, or the contractor's approved site safety plan if more stringent, and report to either the on-scene manager/coordinator or the contractor's safety officer. The safety and health of the public and on-site personnel and the protection of the environment will take precedence over cost and schedule considerations for all project work.

RESPONSIBILITIES

A. On Scene Manager/Coordinator

The manager has the following responsibilities:

1. Assuring that appropriate personal protective equipment is available and properly utilized by all state personnel.
2. Assuring that personnel are aware of the provisions of this plan and are instructed in the work practices required to ensure safety and in planned procedures for dealing with emergencies.
3. Assuring that personnel are informed of the potential hazards associated with site operations.
4. In conjunction with the safety officer, monitoring of safety performance by all personnel to ensure that proper work practices, as determined by the safety officer are employed.
5. Immediately correcting any improper work practices and/or conditions that may result in injury to personnel or exposure to hazardous conditions.

B. Safety Officer

The Safety Officer has the following responsibilities:

1. The safety officer will be responsible for the implementation, enforcement and monitoring of the safety and health plan.
2. Conducting on-site evaluations of personnel hazards to determine the degree of hazard present.
3. Determine the level of personnel protection and the necessary equipment to insure the safety of all site personnel.
4. Monitoring hazard levels during on-site operations and changing, as necessary, the protection levels and working conditions of site personnel.
5. Monitoring the safety performance of all personnel to insure that the proper work practices are employed.
6. Conducting pre-entry indoctrinations of all on-site personnel with regard to this plan and other safety requirements to be observed during site work, including potential hazards, personal hygiene principles, personnel protective equipment usage and fit testing, and emergency

procedures dealing with fire and medical situations. The safety officer will be responsible for ensuring that personnel not successfully completing the required training are not permitted to perform work on this site.

PRELIMINARY SITE ORGANIZATION

A Contact with local officials. Prior to the commencement of on-site activity the appropriate local officials shall be notified.

B. Establishment of emergency contingency and evacuation plans. Prior to the commencement of on-site activity, plans shall be instituted describing the procedure for evacuation of personnel due to injury. Directions to local hospitals and a map showing location, and emergency phone numbers shall be available and become part of the site-specific work plan. See appendix C

DETERMINATION OF ZONES OF CONTAMINATION

In order to deal with the potential dangers of exposure at this site, three zones will be used to delineate the degree of hazard. The three zones are:

1. Contamination Zone,
2. Intermediate Zone (Decontamination Zone) , and
3. Clean Zone.

Contamination Zone

This shall include all working areas where there is potential for exposure of personnel to contaminated water, soil, and other materials. The required level of personal protection, as previously determined by the safety officer, will be worn at all times by all personnel in the contamination zone. Any "breaks" in the protective system or malfunctions in the equipment shall be reported to the safety officer. No eating, drinking, or smoking shall be permitted in the contamination zone.

Intermediate zone

The intermediate zone serves as a contamination reduction area and is located between the contamination zone and the clean area. Personnel entering the Intermediate zone shall wear protective clothing and carry the respiratory protection required for entry within the Contamination zone. Personnel working within the Intermediate zone shall remain cognizant of the Contamination zone boundaries in order to be prepared for any need to increase their level of protection within the Intermediate zone. A decontamination station will be located at the outer perimeter of the Intermediate zone. All personnel who have been within the Contamination zone shall pass through a decontamination procedure prior to re-entering the Clean zone. Decontamination will be in accordance with the decontamination SOP. See Appendix B.

Clean zone

The Clean zone is the outer area and may be considered to be clear of contamination potential. The command post will be located within the Clean Zone, upwind if possible.. The command post will serve as the site manager/coordinators headquarters and will be equipped with: 1. Communications, 2. Site work plan, 3. First aid supplies, 4. Analytical equipment, 5. Safety equipment.

OFF SITE CONTINGENCY PLAN

This plan shall be developed by state and local officials to allow immediate response to site occurrences requiring assistance of local agencies and shall be available as part of the site work plan.

ON SITE CONTINGENCY PLAN

In the event of injury to on-site personnel or contact with hazardous materials, the following protocol shall be followed.

1. In the event of injury: Notify the safety officer and the site manager.
2. Contact off-site emergency medical facilities and describe injury.
3. Determine extent of injury and perform first aid for life threatening types of injuries-eg. arterial bleeding, respiratory difficulty.
- 4 For other types of injuries, decontaminate prior to administering first aid.
5. Transport personnel to prescribed treatment facility along predetermined routes.

In the event of significant release of toxic or hazardous vapors from any container, well, or excavation, the source of such vapors shall be immediately backfilled, covered with fill or capped. Equipment operators shall utilize SCBA's during such operations. Alternate plans for that portion of site work shall be developed and submitted to the site manager prior to recommencing work in the area.

On-site emergencies, if encountered, can be expected to result from fire/chemical reaction of tank or drum contents, personal casualty, or any combination of the above. If an incident occurs necessitating an emergency response, the site manager will sound an air horn in a predetermined pattern. When the signal is heard, all personnel will assemble at the decontamination station to receive instructions and special safety equipment, if necessary.

If weather deteriorates to the point where the site manager believes work should cease, he/she will sound the air horn in a predetermined pattern in order to stop operations. The crew upon hearing the signal will assemble at the decontamination station.

If a fire emergency occurs, the crew will be signaled to assemble at the decontamination station, and await further instructions. The site manager will notify the appropriate fire and police personnel as spelled out in the site work plan. Firefighting materials on-site will include 2 9lb halon fire extinguishers.

Personal injury would most likely result from either chemical contamination, heat related problems, physical injury from accidents (i.e. falling, lacerations, etc.) in performing the work, or a combination of one or more of the above. The appropriate action depends on the type of injury involved with the priority being to assist the casualty as soon as possible without endangering other personnel. All injuries should be treated with the appropriate first-aid measures and follow-up medical attention if necessary. The injured worker(s) shall immediately move out of the contamination zone or, if necessary be moved out by fellow workers as soon as possible. The site manager and safety officer shall be notified immediately and shall recommend further measures as needed.

In the event that movement to a hospital is necessary, the following information must accompany the employee. 1. The name and telephone number of the employee's family doctor. and 2. an accurate description of the incident including an identification of any chemicals involved, if the incident resulted from chemical exposure, and any symptoms observed following the problem. This information shall be prepared by the safety officer.

DETERMINATION OF THE LEVEL OF PROTECTION

It is important the personnel protective equipment and safety requirements be appropriate to protect against the potential hazards at the site. Protective equipment should be selected based on the type(s), concentration(s), possibilities, and routes of exposure (i.e. inhalation, skin contact, skin absorption, and ingestion).

The level of hazard will be determined by periodic monitoring of the site for contamination by the safety officer and the appropriate level of protection shall be posted at both the command post and the decontamination station. Upgrading the level of protection is at the discretion of the safety officer based on the results of the monitoring.

The level of protection will be determined by the most hazardous situation to be encountered at the site and will be at least as stringent as those in the EPA recommended safety plan.

The site safety officer will ensure that all on-site personnel are equipped with appropriate personal safety equipment and protective clothing. The safety officer will also ensure that all safety equipment is kept clean and well maintained.

APPENDIX A

LEVELS OF PROTECTION

Level A

Personal protection equipment

1. Positive pressure SCBA (MSHA/NIOSH approved) operated in the positive pressure mode.
2. Totally encapsulating suit (boots and gloves attached)
3. Gloves-inner (tight fitting and chemical resistant)
4. Boots-chemical protective, steel toe and shank, depending on suit boot construction; worn over suit boot.
5. Gloves-outer, chemical-resistant. Depending on suit construction shall be worn over suit gloves. May be replaced with tight-fitting, chemical resistant gloves worn inside suit gloves.
6. Underwear-cotton, long-john type*
7. Hard hat* Under suit
8. Disposal protective suit, gloves, and boots, worn under or over encapsulating suit.
9. Coveralls * under suit.
10. 2-way radio communicator.

Criteria for use: When the type(s) and concentration (s) of toxic substances are known and require the highest level of combined protection to the respiratory tract, skin, and eyes, level A shall be used. These conditions would be:

A. Atmospheres which are immediately dangerous to life and health (IDLH) IDLH's can be found in the NIOSH/OSHA's Pocket Guide to Chemical Hazards and/or other references.

B. Known atmospheres of potential situations that would affect the skin or eyes, or could be absorbed into the body through these surfaces in toxic quantities. Potential situations are those where vapors may be generated or splashing may occur through site activities. Standard reference books should be consulted to obtain concentrations hazardous to skin, eyes, or mucous membranes.

At sites where the types and/or potential concentration of toxic substances are unknown.

A. Unless circumstances strongly indicate otherwise, the site should be presumed to present hazards to the respiratory system, skin, and eyes. Level A protection would provide the highest level of protection for the initial entry team. Such mitigating circumstances might be:

1. Environmental measurements contiguous to the site.
2. Reliable, accurate, historical data.
3. Open, unconfined areas.
4. Minimal probability of vapor's presence or splashing with cutaneous affecting substances.

B. In enclosed areas such as buildings, railroad cars, ships holds, etc. level A protection is necessary.

C. When Total vapor readings indicate 500 ppm to 1,000 ppm on instruments such as the photoionizer or organic vapor analyzer

* Optional

LEVEL B

Personal protective equipment

1. Positive pressure SCBA (MSHA/NIOSH approved), operated in the positive pressure mode.
2. Hooded, chemical resistant suit.
3. Gloves, outer, chemical protective.
4. Gloves, Inner, tight fitting, chemical resistant.
5. Boots, outer, chemical protective, heavy rubber disposables.
6. Boots, inner, chemical protective, steel toe and shank.
7. 2-way radio communicator
8. Hard hat*
9. Face shield*

Criteria for use

A. When the type(s) and concentration (s) of hazardous substances are known and require the highest degree of respiratory protection; but a lower level of skin protection.

1. Atmospheres which are immediately dangerous to life and health (IDLH). Type(s) and concentration(s) of vapors in air do not present a hazard to the small unprotected areas of the body.
2. Atmospheres with concentrations of known substances greater than protection factors associated with full-face, air-purifying respirators with appropriate cartridges.
3. Atmospheres with less than 19.5% oxygen.

B. When a determination is made that potential exposure to the body parts not protected by a fully encapsulated suit (primarily neck, ears, etc.) is highly unlikely because of known absence of cutaneous or percutaneous hazards or the activities performed preclude splashing of individuals.

ER 12/16/25
C. Total vapor levels range from 5 ppm on instruments such as the photoionizer or organic vapor analyzer and does not contain suspect high levels of toxic substances affecting skin or eyes.

D. Level B protection is recommended as the lowest level of protection for initial entries until the hazards have been further identified and defined by monitoring, sampling, and other reliable methods of analysis, and personnel protection equipment commensurate with these findings utilized.

LEVEL C

Personal protective equipment

1. Full-face air purifying respirator (MSHA/NIOSH approved)
2. Chemical resistant clothing.
3. Gloves, outer, chemical protective.
4. Gloves, inner, tight fitting, chemical resistant type or woven liners.
5. Hard Hat* (face shield optional)
6. Boots, outer, chemical protective heavy rubber throw-aways.
7. Boots, inner, chemical protective, steel toe and shank.
8. 2-way radio communicator.

Criteria for use

- A. Site known to contain potentially hazardous materials not exceeding air concentrations requiring a protection greater than that afforded by a full or half-face mask or that are at levels that are not harmful to unprotected body area (face, neck, etc.)
- B. Well documented, reliable history of site and patterns of prior entry.
- C. No evidence to suspect acute or chronic toxicity to exposed personnel.
- D. Total vapor reading between 0 ppm and 50 ppm on instruments such as the photoionizer and portable GC
- E. Continuous air or personnel monitoring should occur while wearing Level C protection
- F. Atmosphere contains 19.5% oxygen.

LEVEL D

Personal protective equipment

- 1. Chemical resistant aprons.
- 2. Boots/shoes, safety or chemical resistant steel toed boots.
- 3. Boots, outer, chemical protective heavy rubber throw away.
- 4. Half-face respirators immediately available.
- 5. Safety glasses or safety goggles.
- 6. Gloves

Criteria for use

When there is:

No indication of airborne health hazards present.

No gross indications above background on the photoionizer and/or OVA

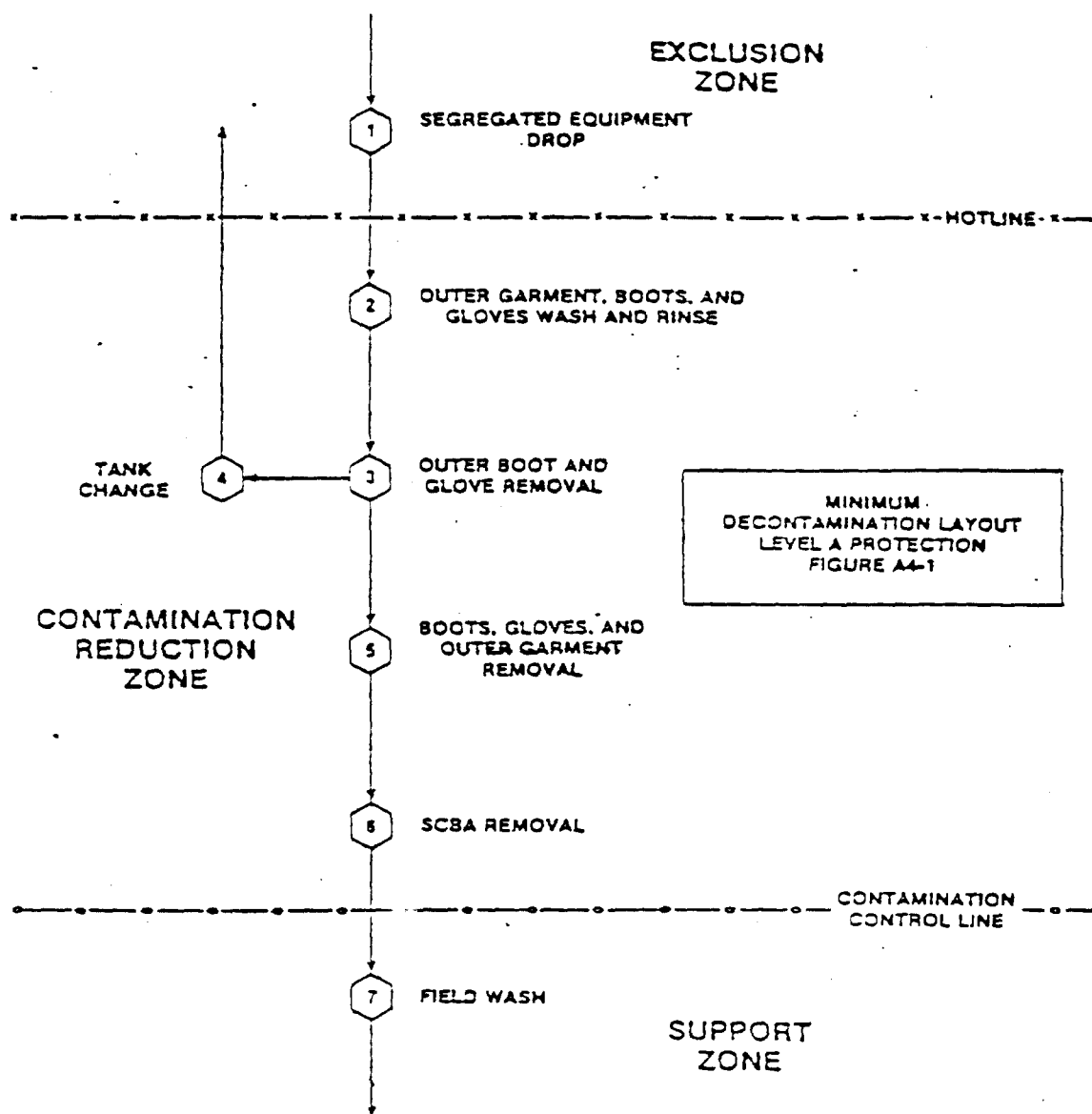
Continuous air or personnel monitoring should occur while wearing level D protection.

APPENDIX B

DECONTAMINATION SOP

COOPERATIVE

The attached document is a copy of the SOP which will be used for all site inspections conducted under the multisite agreement. If site specific differences require a modification of these procedures, that modification will be spelled out in the site work plan.



Equipment: water
soap
tables
wash basin/bucket

ANNEX 4

LEVEL A DECONTAMINATION, MINIMUM LAYOUT

A. EQUIPMENT WORN

The decontamination procedure outlined is for workers wearing Level A protection (with taped joints between gloves, boots, and suit) consisting of:

- Fully encapsulating suit with integral boots and gloves.
- Self-contained breathing apparatus.
- Hard hat (optional).
- Chemical-resistant, steel toe and shank boots.
- Boot covers.
- Inner and outer gloves.

B. PROCEDURE FOR FULL DECONTAMINATION

Station 1: Segregated Equipment Drop

Deposit equipment used on-site (tools, sampling devices and containers, monitoring instruments, radios, clipboards, etc.) on plastic drop cloths or in different containers with plastic liners. Each will be contaminated to a different degree. Segregation at the drop reduces the probability of cross-contamination.

Equipment: various size containers
plastic liners
plastic drop clothes

Station 2: Outer Garment, Boots, and Gloves Wash and Rinse

Scrub outer boots, outer gloves, and fully-encapsulating suit with decon solution or detergent water. Rinse off using copious amounts of water.

Equipment: containers (30-50 gallons)
decon solution
or
detergent water

rinse water
2-3 long-handle, soft-bristle scrub brushes

Station 3: Outer Boot and Glove Removal

Remove outer boots and gloves. Deposit in container with plastic liner.

Equipment: container (30-50 gallons)
plastic liners
bench or stool

Station 4: Tank Change

If worker leaves Exclusion Zone to change air tank, this is the last step in the decontamination procedure. Worker's air tank is exchanged, new outer gloves and boot covers donned, joints taped, and worker returns to duty.

Equipment: air tanks
tape
boot covers
gloves

Station 5: Boot, Gloves, and Outer Garment Removal

Boots, fully-encapsulating suit, and inner gloves removed and deposited in separate containers lined with plastic.

Equipment: containers (30-50 gallons)
plastic liners
bench or stool

Station 6: SCBA Removal

SCBA backpack and facepiece is removed. Hands and face are thoroughly washed. SCBA deposited on plastic sheets.

Equipment: plastic sheets
basin or bucket
soap and towels
bench

Station 7: Field Wash

Thoroughly wash hands and face. Shower as soon as possible.

ANNEX 1

LEVEL A DECONTAMINATION

A. EQUIPMENT WORN

The full decontamination procedure outlined is for workers wearing Level A protection (with taped joints between gloves, boots, and suit) consisting of:

- Fully encapsulating suit.
- Self-contained breathing apparatus.
- Hard hat (optional).
- Chemical-resistant, steel toe and shank boots.
- Boot covers.
- Inner and outer gloves.

B. PROCEDURE FOR FULL DECONTAMINATION

Station 1: Segregated Equipment Drop

Deposit equipment used on-site (tools, sampling devices and containers, monitoring instruments, radios, clipboards, etc.) on plastic drop cloths or in different containers with plastic liners. Each will be contaminated to a different degree. Segregation at the drop reduces the probability of cross-contamination.

Equipment: various size containers
plastic liners
plastic drop cloths

Station 2: Boot Cover and Glove Wash

Scrub outer boot covers and gloves with decon solution or detergent/water.

Equipment: container (20-30 gallons)
decon solution
or
detergent water
2-3 long-handle, soft-bristle scrub brushes

Station 3: Boot Cover and Glove Rinse

Rinse off decon solution from Station 2 using copious amounts of water. Repeat as many times as necessary.

Equipment: container (30-50 gallons)
or
high-pressure spray unit
water
2-3 long-handle, soft-bristle scrub brushes

Station 4: Tape Removal

Remove tape around boots and gloves and deposit in container with plastic liner.

Equipment: container (20-30 gallons)
plastic liners

Station 5: Boot Cover Removal

Remove boot covers and deposit in container with plastic liner.

Equipment: container (30-50 gallons)
plastic liners
bench or stool

Station 6: Outer Glove Removal

Remove outer gloves and deposit in container with plastic liner.

Equipment: container (20-30 gallons)
plastic liners

Station 7: Suit/Safety Boot Wash

Thoroughly wash fully encapsulating suit and boots. Scrub suit and boots with long-handle, soft-bristle scrub brush and copious amounts of decon solution or detergent/water. Repeat as many times as necessary.

Equipment: container (30-50 gallons)
decon solution
or
detergent/water
2-3 long-handle, soft-bristle scrub brushes

Station 8: Suit/Safety Boot Rinse

Rinse off decon solution or detergent/water using copious amounts of water. Repeat as many times as necessary.

Equipment: container (30-50 gallons)
or
high-pressure spray unit
water
2-3 long handle, soft-bristle scrub brushes

Station 9: Tank Change

If worker leaves Exclusion Zone to change air tank, this is the last step in the decontamination procedure. Worker's air tank is exchanged, new outer gloves and boots covers donned, and joints taped. Worker then returns to duty.

Equipment: air tanks
tape
boot covers
gloves

Station 10: Safety Boot Removal

Remove safety boots and deposit in container with plastic liner.

Equipment: container (30-50 gallons)
plastic liners
bench or stool
boot jack

Station 11: Fully Encapsulating Suit and Hard Hat Removal

With assistance of helper, remove fully encapsulating suit (and hard hat). Hang suits on rack or lay out on drop cloths.

Equipment: rack
drop cloths
bench or stool

Station 12: SCBA Backpack Removal

While still wearing facepiece, remove backpack and place on table. Disconnect hose from regulator valve and proceed to next station.

Equipment: table

Station 13: Inner Glove Wash

Wash with decon solution or detergent/water that will not harm skin. Repeat as many times as necessary.

Equipment: basin or bucket
decon solution
or
detergent/water
small table

Station 14: Inner Glove Rinse

Rinse with water. Repeat as many times as necessary.

Equipment: water basin
basin or bucket
small table

Station 15: Facepiece Removal

Remove facepiece. Deposit in container with plastic liner. Avoid touching face with fingers.

Equipment: container (30-50 gallons)
plastic liners

Station 16: Inner Glove Removal

Remove inner gloves and deposit in container with plastic liner.

Equipment: container (20-30 gallons)
plastic liners

Station 17: Inner Clothing Removal

Remove clothing soaked with perspiration. Place in container with plastic liner. Inner clothing should be removed as soon as possible since there is a possibility that small amounts of contaminants might have been transferred in removing fully encapsulating suit.

Equipment: container (30-50 gallons)
plastic liners

Station 18: Field Wash

Shower if highly toxic, skin-corrosive or skin-absorbable materials are known or suspected to be present. Wash hands and face if shower is not available.

Equipment: water
 soap
 small table
 basin or bucket
 field showers
 towels

Station 19: Redress

Put on clean clothes. A dressing trailer is needed in inclement weather.

Equipment: tables
 chairs
 lockers
 clothes

C. FULL DECONTAMINATION (SIT. 1) AND THREE MODIFICATIONS

S I T	STATION NUMBER																		
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
1	X	X	X	X	X	X	X	X		X	X	X	X	X	X	X	X	X	X
2	X	X	X	X	X	X	X	X	X										
3	X						X	X		X	X	X			X	X	X	X	
4	X						X	X	X										

Situation 1: The individual entering the Contamination Reduction Corridor is observed to be grossly contaminated or extremely toxic substances are known or suspected to be present.

Situation 2: Same as Situation 1 except individual needs new air tank and will return to Exclusion Zone.

Situation 3: Individual entering the CRC is expected to be minimally contaminated. Extremely toxic or skin-corrosive materials are not present. No outer gloves or boot covers are worn. Inner gloves are not contaminated.

Situation 4: Same as Situation 3 except individual needs new air tank and will return to Exclusion Zone.

ANNEX 2

LEVEL B DECONTAMINATION

A. EQUIPMENT WORN

The full decontamination procedure outlined is for workers wearing Level B protection (with taped joints between gloves, boot, and suit) consisting of:

- One-piece, hooded, chemical-resistant splash suit.
- Self-contained breathing apparatus.
- Hard hat.
- Chemical-resistant, steel toe and shank boots.
- Boot covers
- Inner and outer gloves.

B. PROCEDURE FOR FULL DECONTAMINATION

Station 1: Segregated Equipment Drop

Deposit equipment used on-site (tools, sampling devices and containers, monitoring instruments, radios, clipboards, etc.) on plastic drop cloths or in different containers with plastic liners. Each will be contaminated to a different degree. Segregation at the drop reduces the probability of cross-contamination.

Equipment: various size containers
plastic liners
plastic drop cloths

Station 2: Boot Cover and Glove Wash

Scrub outer boot covers and gloves with decon solution or detergent/water.

Equipment: container (20-30 gallons)
decon solution
or
detergent water
2-3 long-handle, soft-bristle scrub brushes

Station 3: Boot Cover and Glove Rinse

Rinse off decon solution from Station 2 using copious amounts of water. Repeat as many times as necessary.

Equipment: container (30-50 gallons)
 or
 high-pressure spray unit
 water
 2-3 long-handle, soft-bristle scrub brushes

Station 4: Tape Removal

Remove tape around boots and gloves and deposit in container with plastic liner.

Equipment: container (20-30 gallons)
 plastic liners

Station 5: Boot Cover Removal

Remove boot covers and deposit in container with plastic liner.

Equipment: container (30-50 gallons)
 plastic liners
 bench or stool

Station 6: Outer Glove Removal

Remove outer gloves and deposit in container with plastic liner.

Equipment: container (20-30 gallons)
 plastic liners

Station 7: Suit/Safety Boot Wash

Thoroughly wash chemical-resistant splash suit, SCBA, gloves, and safety boots. Scrub with long-handle, soft-bristle scrub brush and copious amounts of decon solution or detergent/water. Wrap SCBA regulator (if belt-mounted type) with plastic to keep out water. Wash backpack assembly with sponges or cloths.

Equipment: container (30-50 gallons)
 decon solution
 or
 detergent/water
 2-3 long-handle, soft-bristle scrub brushes
 small buckets
 sponges or cloths

Station 8: Suit/SCBA/Boot/Glove Rinse

Rinse off decon solution or detergent/water using copious amounts of water. Repeat as many times as necessary.

Equipment: container (30-50 gallons)
 or
 high-pressure spray unit
 water
 small buckets
 2-3 long-handle, soft-bristle scrub brushes
 sponges or cloths

Station 9: Tank Change

If worker leaves Exclusion Zone to change air tank, this is the last step in the decontamination procedure. Worker's air tank is exchanged, new outer gloves and boots covers donned, and joints taped. Worker returns to duty.

Equipment: air tanks
 tape
 boot covers
 gloves

Station 10: Safety Boot Removal

Remove safety boots and deposit in container with plastic liner.

Equipment: container (30-50 gallons)
 plastic liners
 bench or stool
 boot jack

Station 11: SCBA Backpack Removal

While still wearing facepiece, remove backpack and place on table. Disconnect hose from regulator valve and proceed to next station.

Equipment: table

Station 12: Splash Suit Removal

With assistance of helper, remove splash suit. Deposit in container with plastic liner.

Equipment: container (30-50 gallons)
 plastic liners
 bench or stool

Station 13: Inner Glove Wash

Wash inner gloves with decon solution or detergent/water that will not harm skin. Repeat as many times as necessary.

Equipment: decon solution
 or
 detergent/water
 basin or bucket
 small table

Station 14: Inner Glove Rinse

Rinse inner gloves with water. Repeat as many times as necessary.

Equipment: water
 basin or bucket
 small table

Station 15: Facepiece Removal

Remove facepiece. Avoid touching face with gloves. Deposit in container with plastic liner.

Equipment: container (30-50 gallons)
 plastic liners

Station 16: Inner Glove Removal

Remove inner gloves and deposit in container with plastic liner.

Equipment: container (20-30 gallons)
 plastic liners

Station 17: Inner Clothing Removal

Remove clothing soaked with perspiration. Place in container with plastic liner. Do not wear inner clothing off-site since there is a possibility small amounts of contaminants might have been transferred in removing fully encapsulating suit.

Equipment: container (30-50 gallons)
 plastic liners

Station 18: Field Wash

Shower if highly toxic, skin-corrosive, or skin-absorbable materials are known or suspected to be present. Wash hands and face if shower is not available.

Equipment: water
 soap
 small tables
 basins or buckets
 field showers

Station 19: Redress

Put on clean clothes. A dressing trailer is needed in inclement weather.

Equipment: tables
 chairs
 lockers
 clothes

C. FULL DECONTAMINATION (SIT. 1) AND THREE MODIFICATIONS

S I T	STATION NUMBER																		
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
1	X	X	X	X	X	X	X	X		X	X	X	X	X	X	X	X	X	X
2	X	X	X	X	X	X	X	X	X										
3	X						X	X		X	X	X			X	X	X	X	X
4	X						X	X	X										

Situation 1: The individual entering the Contamination Reduction Corridor is observed to be grossly contaminated or extremely toxic substances are known or suspected to be present.

Situation 2: Same as Situation 1 except individual needs new air tank and will return to Exclusion Zone.

Situation 3: Individual entering the CRC is expected to be minimally contaminated. Extremely toxic or skin-corrosive materials are not present. No outer gloves or boot covers are worn. Inner gloves are not contaminated.

Situation 4: Same as Situation 3 except individual needs new air tank and will return to Exclusion Zone.

ANNEX 3

LEVEL C DECONTAMINATION

A. EQUIPMENT WORN

The full decontamination procedure outlined is for workers wearing Level C protection (with taped joints between gloves, boots, and suit) consisting of:

- One-piece, hooded, chemical-resistant splash suit.
- Canister equipped, full-face mask.
- Hard hat.
- Chemical-resistant, steel toe and shank boots.
- Boot covers.
- Inner and outer gloves.

B. PROCEDURE FOR FULL DECONTAMINATION

Station 1: Segregated Equipment Drop

Deposit equipment used on-site (tools, sampling devices and containers, monitoring instruments, radios, clipboards, etc.) on plastic drop cloths or in different containers with plastic liners. Each will be contaminated to a different degree. Segregation at the drop reduces the probability of cross-contamination.

Equipment: various size containers
plastic liners
plastic drop cloths

Station 2: Boot Cover and Glove Wash

Scrub outer boot covers and gloves with decon solution or detergent/water.

Equipment: container (20-30 gallons)
decon solution
or
detergent water
2-3 long-handle, soft-bristle scrub brushes

Station 3: Boot Cover and Glove Rinse

Rinse off decon solution from Station 2 using copious amounts of water. Repeat as many times as necessary.

Equipment: container (30-50 gallons)
or
high-pressure spray unit
water
2-3 long-handle, soft bristle scrub brushes

Station 4: Tape Removal

Remove tape around boots and gloves and deposit in container with plastic liner.

Equipment: container (20-30 gallons)
plastic liners

Station 5: Boot Cover Removal

Remove boot covers and deposit in container with plastic liner.

Equipment: container (30-50 gallons)
plastic liners
bench or stool

Station 6: Outer Glove Removal

Remove outer gloves and deposit in container with plastic liner.

Equipment: container (20-30 gallons)
plastic liners

Station 7: Suit/Safety Boot Wash

Thoroughly wash splash suit and safety boots. Scrub with long-handle, soft-bristle scrub brush and copious amounts of decon solution or detergent/water. Repeat as many times as necessary.

Equipment: container (30-50 gallons)
decon solution
or
detergent/water
2-3 long-handle, soft-bristle scrub brushes

Station 8: Suit/Safety Boot Rinse

Rinse off decon solution or detergent/water using copious amounts of water. Repeat as many times as necessary.

Equipment: container (30-50 gallons)
 or
 high-pressure spray unit
 water
 2-3 long-handle, soft-bristle scrub brushes

Station 9: Canister or Mask Change

If worker leaves Exclusion Zone to change canister (or mask), this is the last step in the decontamination procedure. Worker's canister is exchanged, new outer gloves and boots covers donned, and joints taped. Worker returns to duty.

Equipment: canister (or mask)
 tape
 boot covers
 gloves

Station 10: Safety Boot Removal

Remove safety boots and deposit in container with plastic liner.

Equipment: container (30-50 gallons)
 plastic liners
 bench or stool
 boot jack

Station 11: Splash Suit Removal

With assistance of helper, remove splash suit. Deposit in container with plastic liner.

Equipment: container (30-50 gallons)
 bench or stool
 liner

Station 12: Inner Glove Wash

Wash inner gloves with decon solution or detergent/water that will not harm skin. Repeat as many times as necessary.

Equipment: decon solution
 or
 detergent/water
 basin or bucket

Station 13: Inner Glove Rinse

Rinse inner gloves with water. Repeat as many times as necessary.

Equipment: water
basin or bucket
small table

Station 14: Facepiece Removal

Remove facepiece. Avoid touching face with gloves. Deposit facepiece in container with plastic liner.

Equipment: container (30-50 gallons)
plastic liners

Station 15: Inner Glove Removal

Remove inner gloves and deposit in container with plastic liner.

Equipment: container (20-30 gallons)
plastic liners

Station 16: Inner Clothing Removal

Remove clothing soaked with perspiration. Place in container with plastic liner. Do not wear inner clothing off-site since there is a possibility small amounts of contaminants might have been transferred in removing splash suite.

Equipment: container (30-50 gallons)
plastic liners

Station 17: Field Wash

Shower if highly toxic, skin-corrosive or skin-absorbable materials are known or suspected to be present. Wash hands and face if shower is not available.

Equipment: water
soap
tables
wash basins/buckets
field showers

Station 18: Redress

Put on clean clothes. A dressing trailer is needed in inclement weather.

Equipment: tables
chairs
lockers
clothes

C. FULL DECONTAMINATION (SIT. 1) AND THREE MODIFICATIONS

S I T	STATION NUMBER																	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
2	X	X	X	X	X	X	X	X	X									
3	X						X	X		X	X			X	X	X	X	
4	X						X	X	X									

Situation 1: The individual entering the Contamination Reduction Corridor is observed to be grossly contaminated or extremely skin corrosive substances are known or suspected to be present.

Situation 2: Same as Situation 1 except individual needs new canister or mask and will return to Exclusion Zone.

Situation 3: Individual entering the CRC is expected to be minimally contaminated. Extremely skin-corrosive materials are not present. No outer gloves or boot covers are worn. Inner gloves are not contaminated.

Situation 4: Same as Situation 3 except individual needs new canister or mask and will return to Exclusion Zone.

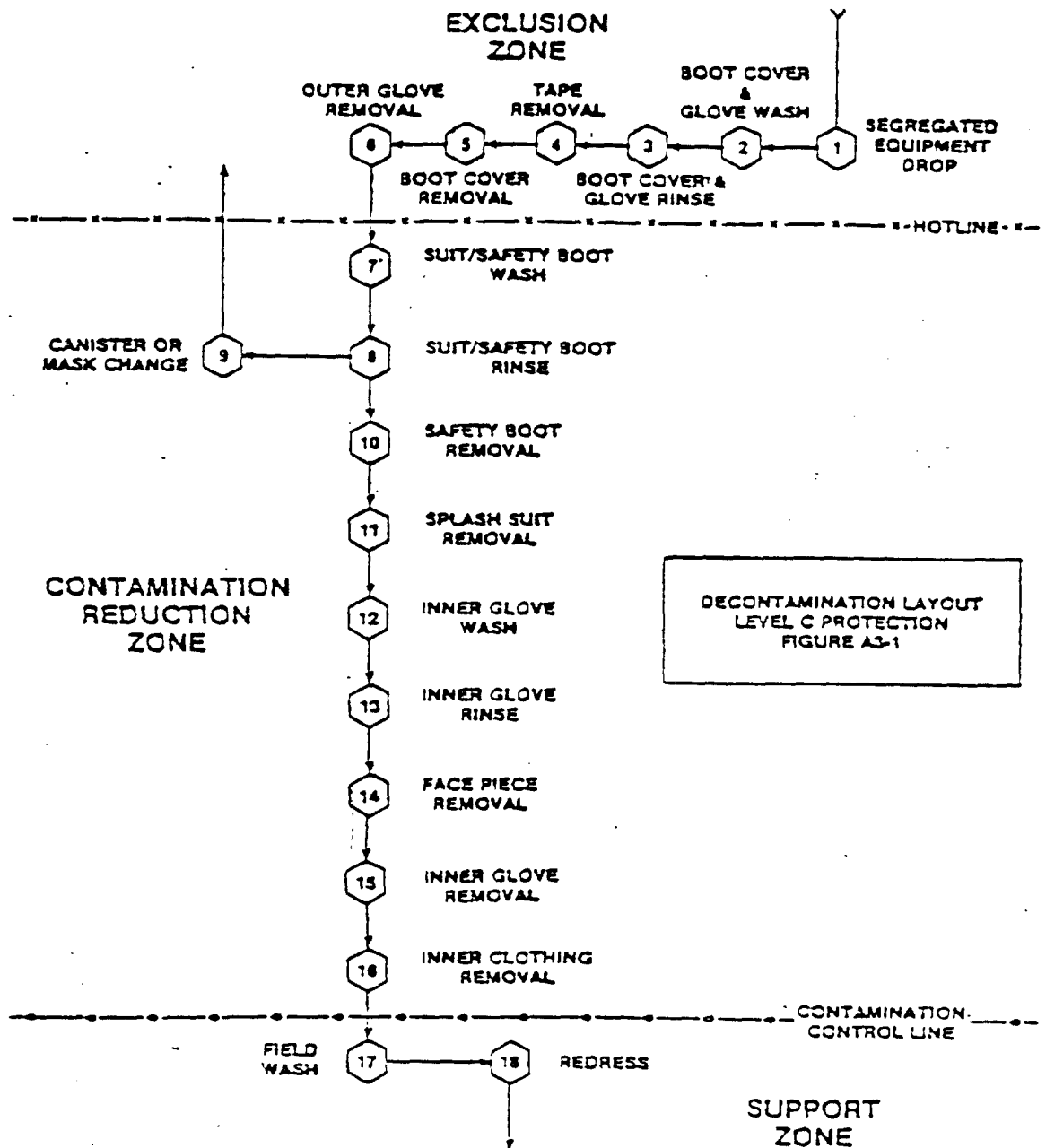


Table 4. Sample Protective Ensembles^a

LEVEL OF PROTECTION	EQUIPMENT	PROTECTION PROVIDED	SHOULD BE USED WHEN:	LIMITING CRITERIA
A	<p>RECOMMENDED:</p> <ul style="list-style-type: none"> • Pressure-demand, full-facepiece SCBA or pressure-demand supplied-air respirator with escape SCBA. • Fully-encapsulating, chemical-resistant suit. • Inner chemical-resistant gloves. • Chemical-resistant safety boots/shoes. • Two-way radio communications. <p>OPTIONAL:</p> <ul style="list-style-type: none"> • Cooling unit. • Coveralls. • Long cotton underwear. • Hard hat. • Disposable gloves and boot covers. 	The highest available level of respiratory, skin, and eye protection.	<ul style="list-style-type: none"> • The chemical substance has been identified and requires the highest level of protection for skin, eyes, and the respiratory system based on either: <ul style="list-style-type: none"> — measured (or potential for) high concentration of atmospheric vapors, gases, or particulates or — site operations and work functions involving a high potential for splash, immersion, or exposure to unexpected vapors, gases, or particulates harmful to skin or capable of being absorbed through the intact skin. • Substances with a high degree of hazard to the skin are known or suspected to be present, and skin contact is possible. • Operations must be conducted in confined, poorly ventilated areas until the absence of conditions requiring Level A protection is determined. 	<ul style="list-style-type: none"> • Fully-encapsulating suit material must be compatible with the substances involved.

Table 4 (Cont.)

LEVEL OF PROTECTION	EQUIPMENT	PROTECTION PROVIDED	SHOULD BE USED WHEN:	LIMITING CRITERIA
B	<p>RECOMMENDED:</p> <ul style="list-style-type: none"> • Pressure-demand, full-facepiece SCBA or pressure-demand supplied-air respirator with escape SCBA. • Chemical-resistant clothing (coveralls and long-sleeved jacket; hooded, one- or two-piece chemical splash suit; disposable chemical-resistant one-piece suit). • Inner and outer chemical-resistant gloves. • Chemical-resistant safety boots/shoes. • Hard hat. • Two-way radio communications. <p>OPTIONAL:</p> <ul style="list-style-type: none"> • Coveralls. • Disposable boot covers. • Face shield. • Long cotton underwear. 	<p>The same level of respiratory protection but less skin protection than Level A.</p> <p>It is the minimum level recommended for initial site entries until the hazards have been further identified.</p>	<ul style="list-style-type: none"> • The type and atmospheric concentration of substances have been identified and require a high level of respiratory protection, but less skin protection. This involves atmospheres: <ul style="list-style-type: none"> — with IDLH concentrations of specific substances that do not represent a severe skin hazard; or — that do not meet the criteria for use of air-purifying respirators. • Atmosphere contains less than 19.5 percent oxygen. • Presence of incompletely identified vapors or gases is indicated by direct-reading organic vapor detection instrument, but vapors and gases are not suspected of containing high levels of chemicals harmful to skin or capable of being absorbed through the intact skin. 	<ul style="list-style-type: none"> • Use only when the vapor or gases present are not suspected of containing high concentrations of chemicals that are harmful to skin or capable of being absorbed through the intact skin. • Use only when it is highly unlikely that the work being done will generate high concentrations of vapors, gases, or particulate or splashes of material that will affect exposed skin.

*Based on EPA protective ensembles.

PERSONAL PROTECTIVE EQUIPMENT

Table 4 (Cont.)

LEVEL OF PROTECTION	EQUIPMENT	PROTECTION PROVIDED	SHOULD BE USED WHEN:	LIMITING CRITERIA
C	<p>RECOMMENDED:</p> <ul style="list-style-type: none"> • Full-facepiece, air-purifying, canister-equipped respirator. • Chemical-resistant clothing (overalls and long-sleeved jacket; hooded, one- or two-piece chemical splash suit; disposable chemical-resistant one-piece suit). • Inner and outer chemical-resistant gloves. • Chemical-resistant safety boots/shoes. • Hard hat. • Two-way radio communications. <p>OPTIONAL:</p> <ul style="list-style-type: none"> • Coveralls. • Disposable boot covers. • Face shield. • Escape mask. • Long cotton underwear. 	The same level of skin protection as Level B, but a lower level of respiratory protection.	<ul style="list-style-type: none"> • The atmospheric contaminants, liquid splashes, or other direct contact will not adversely affect any exposed skin. • The types of air contaminants have been identified, concentrations measured, and a canister is available that can remove the contaminant. • All criteria for the use of air-purifying respirators are met. 	<ul style="list-style-type: none"> • Atmospheric concentrations of chemical must not exceed IDLH levels. • The atmosphere must contain at least 19.5 percent oxygen.
D	<p>RECOMMENDED:</p> <ul style="list-style-type: none"> • Coveralls. • Safety boots/shoes. • Safety glasses or chemical splash goggles. • Hard hat. <p>OPTIONAL:</p> <ul style="list-style-type: none"> • Gloves. • Escape mask. • Face shield. 	No respiratory protection. Minimal skin protection.	<ul style="list-style-type: none"> • The atmosphere contains no known hazard. • Work functions preclude splashes, immersion, or the potential for unexpected inhalation of or contact with hazardous levels of any chemicals. 	<ul style="list-style-type: none"> • This level should not be worn in the Exclusion Zone. • The atmosphere must contain at least 19.5 percent oxygen.

Table 5. Signs and Symptoms of Heat Stress

-
- *Heat rash* may result from continuous exposure to heat or humid air.
 - *Heat cramps* are caused by heavy sweating with inadequate electrolyte replacement. Signs and symptoms include:
 - muscle spasms
 - pain in the hands, feet, and abdomen
 - *Heat exhaustion* occurs from increased stress on various body organs including inadequate blood circulation due to cardiovascular insufficiency or dehydration. Signs and symptoms include:
 - pale, cool, moist skin
 - heavy sweating
 - dizziness
 - nausea
 - fainting
 - *Heat stroke* is the most serious form of heat stress. Temperature regulation fails and the body temperature rises to critical levels. Immediate action must be taken to cool the body before serious injury and death occur. Competent medical help must be obtained. Signs and symptoms are:
 - red, hot, usually dry skin
 - lack of or reduced perspiration
 - nausea
 - dizziness and confusion
 - strong, rapid pulse
 - coma
-

dehydration, obesity, alcohol and drug use, infection, sunburn, chronic disease, and diarrhea. Because heat stress is one of the most common, and potentially serious, illnesses at hazardous waste sites, regular monitoring and preventive precautions are vital. Some of these precautions include adjusting work schedules, providing shelter or shaded areas, and maintaining workers' body fluids by urging them to drink liquids.

VI. QUALITY ASSURANCE PROJECT PLAN

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QUALITY ASSURANCE PROJECT PLAN
FOR THE
SAVAGE MUNICIPAL WELL SITE - MILFORD, NEW HAMPSHIRE

NOVEMBER 1987

New Hampshire Department of Environmental Services
Waste Management Division

Approved:

NHDES-WMD

EPA

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Document Control Number: NH-QC-001

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3.0 Project Description	1	0	Nov. 1987
4.0 Project Organization and Responsibility	1	0	Nov. 1987
5.0 QA Objectives (Insert "A")	1	1	April 1985
6.0 Sampling Collection Procedures and Devices		1	April 1985
7.0 Sample Custody and Documentation	11	11	July 1985
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14.0 Specific Routine Procedures	16	2	July 1985
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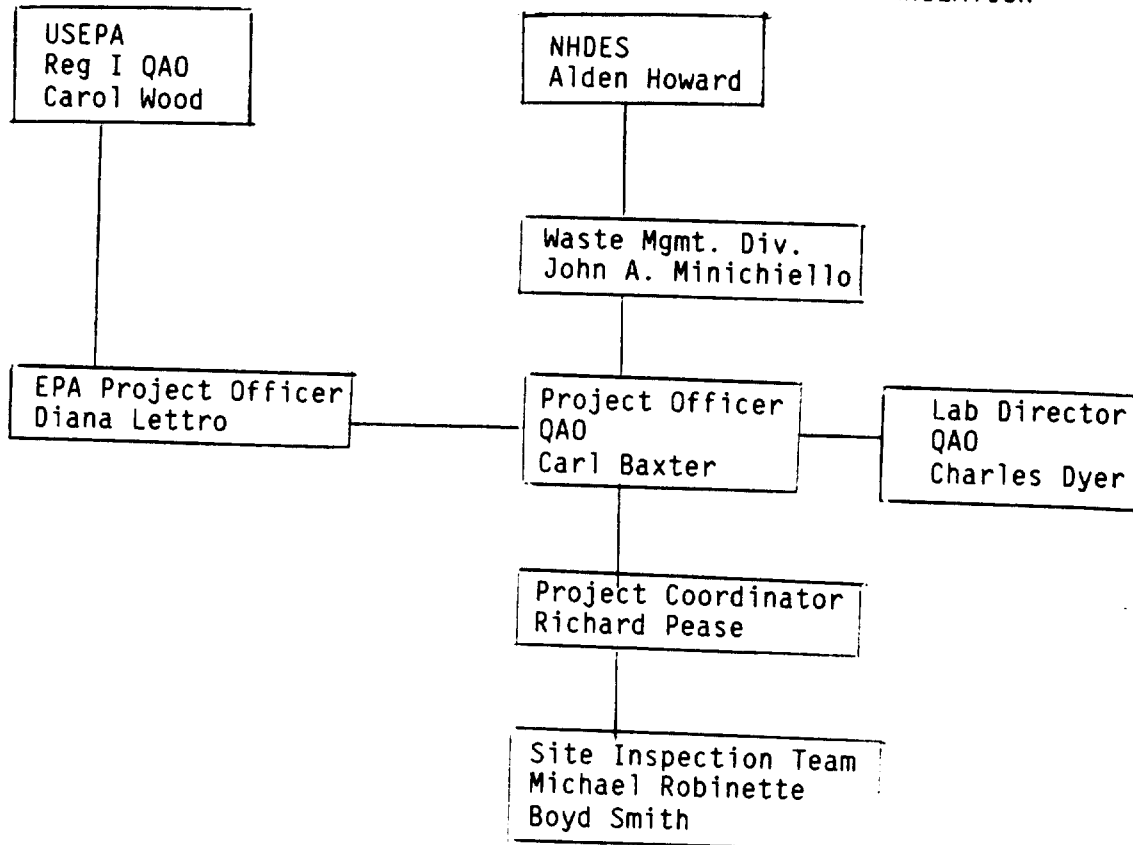
(Insert "A") For measurement data in terms of precision, accuracy, completeness, representativeness, and compatibility, and analytical procedures.

3.0 PROJECT DESCRIPTION

The purpose of the Remedial Investigation/Feasibility Study is to perform the necessary field work and laboratory analyses to define the extent of contamination and potential public health risks so that remedial action alternatives can be evaluated and the most appropriate alternative selected.

New Hampshire Department of Environmental Services (NHDES) support activities provided in this Quality Assurance Project Plan (QAPP) include the analyzing of split samples and confirmatory samples for each sampling episode conducted by the Potentially Responsible Parties' (PRPs) contractor. The purpose of this effort is to ensure the validity of the results reported.

SITE INVESTIGATIONS TABLE OF ORGANIZATION



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QA Objectives for Measurement Data in Terms of
Precision, Accuracy, Completeness,
Representativeness, and Comparability

The New Hampshire QA/QC Project Plan - Section 10.0 addresses precision, accuracy and completeness for each major parameter. This section is a summary index listing the parameters of interest, the analytical method of choice, sample matrix and the NHDES's projections for accuracy and precision. Eventually the accuracy and precision given for each parameter will be based on historical data representative of the media (solid waste, water, industrial waste, etc.), and the conditions being measured. The NHDES does not have sufficient historical data at this time, but this data will be generated for each site, before a project has reached completion. It is solely the project manager's responsibility to assure the adequate and valid quality assurance data is generated before project completion.

It has been the policy of the NHDES Laboratory to calculate data and report it in units, which are recommended by EPA. Since the NHWSPCC Laboratory uses only EPA methods, it is understood by employing these methods the data calculations and units in which the data are expressed will allow for comparability of data bases among organizations.

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6.0 Sampling Procedures

At the request of the NHDES representative, the PRPs contractor shall provide such parallel samples to the NHDES representative in containers using identical or parallel sampling procedures as used in collecting the PRP sample.

7.0 SAMPLE CUSTODY AND DOCUMENTATION

Document Control

All information pertinent to a field survey and/or sampling will be recorded by Commission personnel in various forms: field logbook, sample tags, photographs, maps, etc. Proper documentation and document control are crucial to any future enforcement action since evidence gathered by field and laboratory personnel may become the focal point of any hearing or prosecution.

The purpose of document control is to assure that all documents for a specific project are accountable when the project is completed. Accountable documents include items such as logbooks, field data records, internal and external communications, chain of custody records, laboratory bench logs and analytical records and photographs. Each document should be secured in the appropriate project file.

The specific project manager, officer or on-scene coordinator will be responsible to insure that all records are properly filed. It should be his/her responsibility to insure that a project file removed for inspection, review, copying, etc. is immediately returned to its proper place. A log out-log in system will be used to track any files which leave the immediate vicinity of the file storage area. Under no circumstance should the original file be loaned to non-Commission personnel.

Information discovered or observed during field surveys and/or sampling must be recorded. Field personnel should maintain a logbook or insure that all information is transferred by initialed memorandum to the project officer and the project file. Examples of information to be recorded are:

- Date and time of event
- Purpose of sampling, surveillance
- Names and addresses of personnel present
- Discharger, generator or disposer of waste and address
- Type of process producing waste
- Type of waste or sample (eg., air, sludge, soil, water, other liquid, gas or solid)
- Description of sample
- Number and volume of sample taken
- Description of sampling point
- Time and date of sample collection.
- Collector's name
- References such as maps, photographs
- Field observations (eg., wind, temperature, weather, terrain conditions)
- Any field measurements made such as pH, dissolved oxygen, temperature, conductivity, specific ions, photoionization analysis

Since sampling situations can vary widely, notes should be as descriptive as possible. Recorded information should be sufficient so that someone can reconstruct the sampling situation without reliance on memory.

Photographs are the most accurate demonstration of the field personnel's observations. They can be significant and informative to the field team for review during future inspections, meetings and hearings. Documentation of a photograph is critical to its validity as a representation of an existing situation. Therefore, for each photograph taken, several items should be noted on the photograph or in the field notebook:

- "Date
- Time
- Photographer
- Name of site
- General direction faced and description of subject
- Same measure of scale
- Photograph number

The Commission maintains several 35mm and instant type cameras for on-site documentation. Only lenses that afford a perspective similar to that of the naked eye will be used for enforcement purposes.

Samples

Each sample will be labeled and properly sealed immediately after collection. Sample container tags or labels using waterproof ink should be filled out prior to sample collection.

Sample labels must be firmly affixed to sample containers. Gummed or contact type labels will be used and are to be applied before sample collection. The label should include:

- name of collector and initials
- date and time of collection
- place of collection
- sample number
- field information

A typical sample label is shown in Figure 5.1.

Chain of Custody

As in any other activity that may be used to support litigation, the Commission must be able to provide the chain of possession and custody of any samples which are offered for evidence or which form the basis of analytical test results introduced into evidence in any pollution or public health case. It is imperative that proper procedures are followed whenever evidence samples are collected, transferred, stored, analyzed, or destroyed. The primary objective of these procedures is to create an accurate written record which can be used to trace the possession and handling of the sample from the moment of its collection through analysis and its introduction as evidence.

A sample is in someone's custody if:

- it is in actual physical possession, or
- it remains in view after being in physical possession, or
- it is secured (locked) after being in physical possession, or
- it is restricted to authorized personnel after being secured.

It is important that a minimum number of persons be involved in sample collection and handling. Procedures recorded in this project plan for sample collection preservation and handling will be used. Field records should be completed at the time the sample is collected and should be signed or initialled by the collector and time and date recorded. The standard New Hampshire Water Supply and Pollution Control Commission laboratory analysis sheets should be used. The sheet contains space for recording:

- sample number
- time and date
- source of sample
- sample type (water, soil, sludge)
- preservative used
- analysis required
- name of collector
- pertinent field measurements (ph, D.O., etc.)
- serial number (for lab tracking)

The samples are to remain in the possession of Commission field personnel until transfer to the laboratory. If samples are to be left unattended, they must be placed in a suitable cooler and the lid sealed with gummed tape which would indicate tampering if removed.

When samples arrive at the laboratory, the field crew must log each sample into the computer. Input information is similar to that provided on the laboratory analysis sheet. After log in, custody of the samples are transferred to laboratory personnel using the reverse side of the laboratory analysis sheet. A separate laboratory analysis sheet is used for organic determination. See figures 5-2 and 5-3 for example chain of custody forms.

Once samples are logged in and transferred to laboratory personnel, they are only handled by authorized analysts. If samples are not immediately analyzed, they are placed in an appropriate environment such as a walk in refrigerator. A lockable chest within the refrigerator is available for use for additional security. The laboratory is locked during

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non-working hours. Laboratory log sheets, shown in another section of this project plan, identify each analyst working on the sample.

The foregoing chain of custody procedure is consistent with published EPA guidelines and has been successfully defended in several enforcement actions. The director of laboratory is charged with periodic review of these procedures and to upgrade them to remain within published guidelines.

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NEW HAMPSHIRE WATER SUPPLY AND POLLUTION
CONTROL COMMISSION SAMPLE

Collector _____ Collector's Sample No. _____

Place of Collection _____

Date Sample _____ Time Sampled _____

Field Information _____

Figure 5-1. Sample Label



State of New Hampshire
DEPARTMENT OF ENVIRONMENTAL SERVICES
WASTE MANAGEMENT DIVISION

6 Hazen Drive, Concord, NH 03301
603-271-4474

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SOLID WASTE COM
VACANT, Chair
ROBERT WHEELER, Vice
MARILYN ANDREWS
WILLIAM ARNOLD
PAUL BISHOP, Ph.D.
ROBERT BURROW
RICHARD GROSSMAN
JOHN ISHAM
WILLIAM JENNES
JOHN LAFALLEE
PHILIP MACALLISTER
FREDERICK MCGARR
JOHN OSGOOD

ALDEN H. HOWARD
COMMISSIONER

John A. Minichiello
Assistant Director

CHAIN OF CUSTODY

Site/Location/Code:

Date Samples Collected:

Date Sample Received:

<u>Sample Number</u>	<u>Description</u>
a.	
b.	
c.	
d.	
e.	
f.	
g.	
h.	
i.	
j.	

Persons(s) and Division Relinquishing Samples:

Person(s)/ Lab Receiving Samples:

Date Samples Analyzed:

Analyst(s):

Notebook and/or Reference Number:

Additional Comments:

NEW HAMPSHIRE WATER SUPPLY AND POLLUTION CONTROL COMMISSION
LABORATORY ANALYSIS

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Station # _____ SAMPLED COLLECTED By: _____ Date: _____ Time: _____		Source: _____ LOCATION: _____ _____ _____		Lab # _____ RECEIVED IN LAB By: _____ Date: _____ Time: _____			
All results in mg/l unless otherwise noted							
ON SITE OBSERVATIONS	DEPTH (Sample): M			PHYSICAL/MINERAL ANALYSES	ALKALINITY, CaCO ₃ :		
	FLOW: L-M-H (cfs)				CHLORIDE, Cl:		
	SALINITY: o/oo				COLOR (Apparent): Units		
	SECCHI DISC: cm				FLUORIDE, F:		
	TEMPERATURE (Air): °C				HARDNESS, CaCO ₃		
	TEMPERATURE (Sample): °C				pH: Units		
	WEATHER: Std Abbr				SPEC. CONDUCT: µMHOS		
	REMARKS:				SILICA, DIS, SiO ₂ :		
			SULFATE, SO ₄				
			SULFIDE, S:				
			SULFITE, SO ₃ :				
			TURBIDITY: NTU				
BIOLOGICAL ANALYSES	CHLOROPHYL "A": mg/M ³			RESIDUE ANALYSES	FIXED (105°)		
	COLIFORM, TOT: MPN/100ml				TOTAL:		
	COLIFORM, TOT: cts/100ml				FILTERABLE (Dis)		
	COLIFORM, FECAL: cts/100ml				NON-FILTERABLE (Susp):		
	FECAL STREP: cts/100ml				SETTLABLE: ml/L/Hr		
DETRITUS ANALYSES	BOD				ORGANIC ANALYSES	VOLATILE (550°C)	
	COD					TOTAL:	
	OXYGEN, DIS					FILTERABLE (Dis):	
	TOC					NON-FILTERABLE (Susp):	
NUTRIENT ANALYSES	NITROGEN, TKN, N:					SPECIAL ANALYSES (See Sep. Shit.)	CYANIDE, CN:
	NITROGEN, NH ₃ , N:			MBAS (Surfactants):			
	NITROGEN, NO ₂ +NO ₃ , N:			OIL & GREASE (Freon Ext):			
	PHOSPHATE, DIS, ORTHO, P:			PHENOLICS, Phenol:			
	PHOSPHORUS, TOTAL, P:						
METALS ANALYSES	ALUMINUM, Al:			NOTES.		PLANKTON	
	ARSENIC, As:				ORGANICS (Qualitative)		
	BARIUM, Ba:				PESTICIDES		
	CADMIUM, Cd:				RADIOLOGICAL		
	CALCIUM, Ca:				OTHERS (Specify):		
	CHROMIUM, Cr:						
	COPPER, Cu:						
	IRON, Fe:						
	LEAD, Pb:						
	MAGNESIUM, Mg:						
	MANGANESE, Mn:						
	MERCURY, Hg:						
	NICKEL, Ni:						
	POTASSIUM, K:						
	SELENIUM, Se:						
	SILVER, Ag:						
	SODIUM, Na:						
	TIN, Sn:						
	ZINC, Zn:						
					RESULTS REVIEWED IN LAB		
				By: _____ Date: _____			
				COMMENTS:			
				COPY TO: _____ Date: _____			

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Calibration Procedures and Frequency

The purpose of this section is to document by reference to appropriate standard operating procedures, methods which are employed to assure that field and laboratory equipment are functioning properly. The application of the calibration procedures noted below are routinely recorded in the equipment logs.

Consult the individual laboratory analytical procedures for information concerning:

- (1) Frequency of recalibration
- (2) The source of calibration Standards and Quality Control Standards.
- (3) The proper dilutions of these standards to use for calibration and quality control purposes.
- (4) The instrument system used for the analysis.
- (5) The references for the procedure employed.

Procedures for laboratory analytical equipment are located in Section 10 of the Quality Assurance Plan.

FIELD EQUIPMENT

pH Meter

1) Purpose

To provide operating procedures for Orion Research analog pH meter model 399A

2) Equipment and Materials

- Pre-cleaned jars
- Three pH laboratory buffer solutions with pH's of 4.0, 7.0, and 10.0
- Distilled or de-ionized water
- Squeeze bottle
- Clean paper towels
- VWR Scientific, Inc. digital pH/mv meter (with battery fully charged)
- Meter operation and maintenance instruction manual

3) Procedures

A) Two-buffer standardization

This procedure is recommended for precise measurements or for checking electrode operation.

1. Place electrode in a beaker of distilled water and stir vigorously. Remove and shake off drops of water.
2. Place electrode in a buffer near pH 7 and stir vigorously. Stop stirring and wait for a stable reading (less than 30 seconds should be required).
3. Set the meter to the pH of the buffer with the calibration control.
4. Place electrode in a beaker of distilled water and stir vigorously. Remove and shake off drops of water.

5. Place electrode in a buffer which is at least 3 pH units from the first buffer and which is near sample pH (e.g., pH 4 for acidic samples or pH 10 for basic samples) and stir vigorously. Stop stirring and wait for a stable reading.
6. Set the meter reading to the pH of the buffer with the temperature compensator knob. Turn the plastic slope indicator until the arrow on the temperature knob points to the buffer temperature. The percent slope, when on the bottom half of the indicator, should be greater than 90%. If not, see Cleaning Procedure.
7. Remove electrode and place in a beaker of distilled water. Stir vigorously. Remove and shake off drops of water, place in sample, and stir vigorously.
8. Stop stirring and wait for a stable reading. Read sample pH.

4) Documentation

All field readings should be recorded in the field log immediately following the field measurements.

5) References

Instruction Manual, Orion Research Inc., 380 Putnam Avenue, Cambridge, Massachusetts 02139

Conductivity Meter

1) Purpose

To provide procedures for the Yellow Springs Instrument Co., Inc. Model 33 conductivity meter in order to measure the specific conductance of a water sample in the field.

2) Equipment and Materials

- Pre-cleaned jars
- Standard solution of 12.880 uS/cm at 25°C
- Distilled or de-ionized water
- Squeeze bottle
- Clean paper towels
- VSI Model 33 Conductivity Meter (with battery fully charged)
- Meter operation and maintenance instruction manual

3) Procedures

- A. Check the instrument according to specified procedures in the manufacturer's instruction manual.
- B. Calibrate the conductivity meter, following calibration procedures outlined in the instruction manual and using standard solution.
- C. Avoid calibrating on one meter range and making measurements on another.
- D. Maintain calibration solution and sample at the same temperature.

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- E. Quickly stir sample prior to placement of cell in sample.
- F. Place rinsed cell in sample solution and record digitized conductance reading. Measure specific conductance immediately after sampling.

4) Documentation

Record all readings in the field log immediately following the field measurements.

5) References

Yellow Springs Instrument Co., Inc. Model 33 Conductivity Meter
Instruction Manual, Yellow Springs, Ohio

Photoionization Detector (HNU Meter)

1) Purpose

To provide operating procedures for the HNU Systems Model PI 101 photoionization detector for field surveying of organic vapors.

2) Equipment and Materials

HNU Systems Model PI 101 Photoionization Detector

3) Procedures

A. Preparation for use.

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- 1) Assemble the photoinization probe by screwing the handle to the probe body and inserting the probe extension into the probe body.
- 2) Connect the probe to the meter by matching the alignment keys on the 12 pin connector, pressing down, and twisting the connector lock until a distinct snap is felt.
- 3) Turn the function switch to the battery check position. The needle should swing into or above the green arc on the scaleplate. If it does not, the unit must be recharged before use.
- 4) Turn the function switch to the standby position and rotate the zero potentiometer until the meter reads zero. At this setting, the probe fan should turn on, and the UV light source should be on. A distinct hum indicates operation of the fan, while a purple glow in the probe tube indicates UV light source is operational.
- 5) Turn the function switch to the 0-20 ppm scale setting. The meter needle should read between 0.5-0.7 ppm.

B. Operation

- 1) The probe should be held in close proximity to the area being monitored to provide the most accurate reading. The lowest possible scale range should also be selected. In environments where levels of volatile organics are unknown, initially use the 0-2000 ppm scale and then change to lower scales if appropriate.

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- 2) Do not allow the probe intake to directly contact soil or liquid materials. This will disrupt the air flow to the UV light source and may contaminate the probe.

4. Special Notes

- A. For general monitoring in environments where gas mixtures are present, the span adjustment should be set at 9.8.
- B. This instrument will not detect methane or other natural gases.

5. Calibration

Instruments are laboratory calibrated during routine maintenance. During projects requiring repeated use of the meter for more than one day, calibration will be checked in the field daily using a factory-supplied benzene gas.

The calibration gas is supplied by HNU Systems, Inc. Cat. No. 101-350 67ppm at 9.8 span with 10.2 eV source. At these settings, a direct

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connection is made from the gas canister to the probe intake and the zero knob is adjusted until the correct gas concentration is read.

6) Documentation

Readings will be recorded in the field log immediately following the field measurements.

7) Applicable Standards and References

Instruction Manual for Model PI 101 Photoionization Analyzer, HNU Systems, Inc.

INTRODUCTION

This section of the New Hampshire QA/QC Project Plan is devoted to an index summary of the analytical procedures, employed by the New Hampshire Department of Environmental Services. This index references the specific analytical procedure used to determine an analyte of interest, in a particular sample matrix. Further information as to the technique employed and the working range of the instrument-when calibrated in accordance with the method cited-are provided. The laboratory's projected minimal detection limits, Percent bias and Precision are also given in the index.

The projected MDL, % Bias and % Precision, which are cited in the index, were either abstracted from the given reference or developed by the NHDES Laboratory as noted. The NHDES Laboratory generated the data, used to determine the projected MDL, % Bias and % Precision, by spiking the standards of interest into DI water (or organic-free water when appropriate) and analyzing ten times. The method used to calculate the MDL, % Bias and % Precision is outlined in Section No. 16.0 of the NH QA/QC PP. It should be further noted that the projected figures apply to all the sample matrices, unless otherwise noted - (ie waste, surface, ground, and saline waters and solid waste, sludges and slurries). It is recognized that the MDLS, accuracy and precision data may be radically different for each sample matrix. It is anticipated that as a project site develops, the real MDLS, precision and accuracy data will be supplied for each sample matrix pertinent to that specific site. In order to accomplish this the Project Manager must interface with the Laboratory Director and Unit Supervisors to determine the necessary number of field replicates and spike samples required to estimate valid accuracy and precision data. It is the Project Manager's responsibility to assure that adequate and valid precision data are being developed for each site under his jurisdiction. Eventually this index will be modified to reflect the parameters of interest for each site, and the MDL, precision and accuracy for each sample matrix at a specific site.

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MEASUREMENS / PARAMETERS VOLATILE ORGANIC COMPOUNDS: (Purgeables)	ANALYTICAL METHOD	SAMPLE CHARACTERIZATION	TECHNIQUE EMPLOYED	COM- PLETE- NESS	(mg/l) M.D.L.'S (ug/l)	PERCENT BIAS	PERCENT PRECISION
1. Methylene chloride	NIQA/OCCP Section No. 10.46 Nov. 1984 OR NIQA/OCCP Section No. 10.45	Solid Waste, Sludges and Sturries	GC Screen (FID) GC/MS Confirm	100% 100%	QUALITATIVE 2.8	ONLY +7.1	+ 5.2
2. Trichlorofluoromethane			GC Screen (FID) GC/MS Confirm	100% 100%	QUALITATIVE 9.6	ONLY -14.8	±4.6
3. 1, 1-Dichloroethane			GC Screen (FID) GC/MS Confirm	100% 100%	QUALITATIVE 4.5	ONLY -8.9	± 6.2
4. Trans-1,2 Dichloroethane			GC Screen (FID) GC/MS Confirm	100% 100%	QUALITATIVE 5.4	ONLY 18.2	4.1
5. Chloroform			GC Screen (FID) GC/MS Confirm	100% 100%	QUALITATIVE 6.0	ONLY 9.3	5.2
6. 1, 2 Dichloroethane		Ground, Surface and Potable Water	GC Screen (FID) GC/MS Confirm	100% 100%	QUALITATIVE 4.5	ONLY 8.7	3.3
7. 1,1,1 Trichloroethane			GC Screen (FID) GC/MS Confirm	100% 100%	QUALITATIVE 3.4	ONLY 7.0	4.6
8. Carbon Tetrachloride			GC Screen (FID) GC/MS Confirm	100% 100%	QUALITATIVE 3.1	ONLY ≤ 1	6.6
9. Bromodichloromethane			GC Screen (FID) GC/MS Confirm	100% 100%	QUALITATIVE 6.2	ONLY 1.6	5.6
10. 1, 2 Dichloropropane			GC Screen (FID) GC/MS Confirm	100% 100%	QUALITATIVE 5.7	ONLY 8.6	7.7

** Projected = All M.D.L.'s; % Bias and % Precision developed for NI QA/QC PP analytical methods were generated by spiking the standard(s) of interest into DI water and subsequently analyzed ten times. (Refer to Section No. 16.0, for information concerning the actual calculation Wastewater = Industrial and Municipal Wastewater, unless otherwise noted.
N/D = Not Determined
N/A = Not Applicable

MEASUREMENTS / PARAMETERS VOLATILE ORGANIC COMPOUNDS: (Purgeables)	ANALYTICAL METHOD	SAMPLE CHARACTERIZATION	TECHNIQUE EMPLOYED	COM- PLET- NESS	(mg/l) M.D.L.'S (µg/l)	PERCENT BIAS	PERCENT PRECISION
11. Trans-1, 3 Dichloro- propene			GC Screen (FID) GC/MS Confirm	100% 100%	QUALITATIVE 19.7	ONLY 7.6	6.5
12. Trichloroethene			GC Screen (FID) GC/MS Confirm	100% 100%	QUALITATIVE 3.7	ONLY 9.3	4.7
13. Benzene			GC Screen (FID) GC/MS Confirm	100% 100%	QUALITATIVE 3.8	ONLY 4.9	3.4
14. Dibromochloromethane	NHQA/QC/P Section No. 10.45 Nov. 1984	Ground, Surface & Potable Water	GC Screen (FID) GC/MS Confirm	100% 100%	QUALITATIVE 5.2	ONLY 5.8	4.6
15. 1,1,2 Trichloroethane			GC Screen (FID) GC/MS Confirm	100% 100%	QUALITATIVE 4.7	ONLY 26.6	6.1
16. cis-1,3 Dichloropropene			GC Screen (FID) GC/MS Confirm	100% 100%	QUALITATIVE N/D	ONLY 4.8	5.8
17. Bromoform			GC Screen (FID) GC/MS Confirm	100% 100%	QUALITATIVE 4.4	ONLY 10.6	6.1
18. Tetrachloroethane	NHQA/QC/P Section No. 10.46 Nov. 1984	Solid Waste, Sludges, and Sturries	GC Screen (FID) GC/MS Confirm	100% 100%	QUALITATIVE 3.1	ONLY 12.6	3.9
19. Toluene			GC Screen (FID) GC/MS Confirm	100% 100%	QUALITATIVE 3.6	ONLY 2.3	4.6
20. Chlorobenzene			GC Screen (FID) GC/MS Confirm	100% 100%	QUALITATIVE 3.7	ONLY 9.3	4.7
21. Ethyl benzene			GC Screen (FID) GC/MS Confirm	100% 100%	QUALITATIVE 3.2	ONLY 2.3	5.0
22. m-Dichlorobenzene			GC Screen (FID) GC/MS Confirm	100% 100%	QUALITATIVE 8.5	ONLY 10.1	7.3
23. 1,3-Dichlorobenzene			GC Screen (FID) GC/MS Confirm	100% 100%	QUALITATIVE 6.6	ONLY 8.1	8.6
24. 1,4-Dichlorobenzene			GC Screen (FID) GC/MS Confirm	100% 100%	QUALITATIVE N/D	ONLY 7.9	6.8

** Projected = All M.D.L.'s; % Bias and % Precision developed for NH QA/QC PP analytical methods were generated by spiking the standard(s) of interest into DI water and subsequently analyzed ten times. (Refer to Section No. 16.0, for information concerning the actual calculations.
Wastewater = Industrial and Municipal Wastewater, unless otherwise noted.
N/D = Not Determined
N/A = Not Applicable

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MEASUREMENTS / PARAMETERS VOLATILE ORGANIC COMPOUNDS: (Purgeables) 2b. p-xylene	ANALYTICAL METHOD	SAMPLE CHARACTERIZATION	TECHNIQUE EMPLOYED	COM- PLETE- NESS	M.D.L.'s (g/l)	PRECISE BIAS	REPORT DEFLECTION
2b. m-xylene	MMDA/QC/P Section No. 10.45 Nov. 1984	Ground, Surface and Potable Water	GC Screen (FID) GC/MS Confirm	100%	QUALITATIVE 9.4	ONLY -11.6	±5.6
27. o-xylene	MMDA/QC/P Section No. 10.46 Nov. 1984	Solid Waste, Sludges and Sturries	GC/MS Confirm GC/MS Confirm GC/MS Confirm GC/MS Confirm	100% 100% 100% 100%	QUALITATIVE 3.8 QUALITATIVE 4.2 QUALITATIVE 12.6	ONLY -1.7 ONLY -11.5 ONLY -18.7	±5.1 ±4.7 ±6.1
29. Acrylonitrile	Reference 1 Method 624 1982	Ground Surface and Potable Water	GC/MS	100%	11.9	-30	±12
	Reference 4 Method 8.03 1980	Solid Waste Slurries & Sludges	GC/MS	100%	11.9	-30	±12
	Reference 1 Method 624 1982	Ground Surface and Potable Water	GC/MS	100%	13.4	-30	±15
30. Acrolein	Reference 4 Method 8.03 1980	Solid Waste Slurries & Sludges	GC/MS	100%	13.4	-30	±15

** Projected = All M.D.L.s; % Bias and % Precision developed for NH QA/QC PP analytical methods were generated by spiking the standard(s) of interest into DI water and subsequently analyzed ten times. (Refer to Section No. 16.0, for information concerning the actual calculations.
Wastewater = Industrial and Municipal Wastewater, unless otherwise noted.
N/D = Not Determined
N/A = Not Applicable

MEASUREMENTS / PARAMETERS VOLATILE ORGANIC COMPOUNDS (Continued)	ANALYTICAL METHOD	SAMPLE CHARACTERIZATION	TECHNIQUE EMPLOYED	COM- PLET- NESS	M.D.L.'s	PERCENT BIAS	PRECISION
32. Trichloromethane (a) Chloroform (b) Dichlorobromomethane (c) Dibromochloromethane (d) Bromoform	NHQA/UCPP Section No. 10.43 Nov. 1984	Potable Water	GC/MS	100% 100% 100% 100%	(a) 6.0 ug/l (b) 6.2 ug/l (c) 5.2 ug/l (d) 4.4 ug/l	(a) +0.3 (b) -1.6 (c) -5.8 (d) -10.6	(a) 15.2 (b) 15.6 (c) 14.6 (d) 16.1
1. Uranium in Drinking Water	NHQA/UCPP Section No. 10.47 May 1985 DC# NH-QC-012	Potable Water	Radiochemical Method	100%	GT 15 pCi/l gross alpha	-1.0%	7.7
2. Radium - 226 in Drinking Water	NHQA/UCPP Section No. 10.48 May 1985 DC# NH-QC-012	Potable Water	Radium Emanation	100%	0.1 pCi/l	-2.0%	7.3
3. Gross Alpha & Gross Beta Radioactivity in Drinking Water	NHQA/UCPP Section No. 10.49 May 1985 DC# NH-QC-012	Potable Water	Screen	100%	4 pCi/l beta 1 pCi/l alpha	-6.0%	2.3

** Projected = All M.D.L.s; % Bias and % Precision developed for NH QA/QC PP analytical methods were generated by spiking the standard(s) of interest into DI water and subsequently analyzed ten times. (Refer to Section No. 16.0, for information concerning the actual calculations)

Wastewater = Industrial and Municipal Wastewater, unless otherwise noted.

N/D = Not Determined

N/A = Not Applicable

STATE OF N.H. WATER POLLUTION CONTROL LABORATORY
STANDARD METHOD FOR DETERMINATION OF: Metals

References:

1. EPA Manual, Metals Section, March 1979, Revised March 1983, Metals-1 thru Metals-29
2. Standard Methods, 16th ed., 1985, Part 300 thru 328 E, pp 143-261
3. Perkin Elmer 560 and 272, AAS Manuals
4. Perkin Elmer HGA 500 Graphite Furnace Manual
5. Perkin Elmer AS-40 Auto Sampler Manual, Furnace
6. Perkin Elmer AS-50 Auto Sampler Manual, Flame
7. METPRO file. On HP 1000 LAS computer

TECHNIQUE USED: Atomic Absorption (See Section B - Techniques below)

A. Sampling Methodology:

1. Preservative: Ultrex Nitric Acid to pH less than 2 (5mL/L)
2. Holding Time: 6 months
3. Required volume: 1000mL
4. Container Type: LPE

B. Technique:

1. A.A. Flame - Al, Ba, Be, Ca, Cr, Cu, Fe, Mg, Mn, Ni, K, Ag, Na, Tl, Zn
2. A.A. Graphite Furnace - Al, As, Cd, Cr, Cu, Pb, Ni, Se, Ag, Sb, V, Mo, Zn
3. Cold Vapor - Hg

C. Sample Preparation:

1. A.A. Flame: Total Metals (Perkin-Elmer 272 instrument)
 - a. Pour 50 mL of sample into a 125mL Erlenmeyer flask.
 - b. Add 2mL of Ultrex HNO₃ and evaporate to near dryness
 - c. Cool, add an additional 2mL Ultrex HNO₃, reheat and reflux sample on hot plate until digestion is complete. (Using additional 2mL aliquots of Ultrex HNO₃ if necessary.
 - d. Add 2.5 mL of 1:1 Ultrex HCl, and warm to dissolve any residue remaining from the evaporation process.
 - e. Return sample to original volume with D.I. water, filtering through a Whatman 934-AH glass fiber filter, if necessary, to remove silicates or other insoluble matter.
 - f. Add Matrix Modifiers, as needed before atomization.
 - 1) Ca & Mg require addition of 1.0mL La Cl₃ per 10mL sample.
 - 2) Al and Ba require addition of 2mL 10% KCl per 100mL sample
 - g. Analyze sample as per instrumental requirement
2. A.A. Graphite Furnace: Total Metals (Perkin Elmer 560 instrument)

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- a. Pour 30mL of sample into a 50mL Erlenmeyer flask.
- b. Add 1.0mL Ultrex HNO_3 and 0.5mL 30% hydrogen peroxide (H_2O_2) and evaporate to near dryness.
Note: Avoid the use of halide acids in all graphite furnace preparation.
- c. Cool, add an additional 1mL Ultrex HNO_3 , reheat and reflux sample on hot plate until digestion is complete. (Use additional 1mL aliquots if necessary)
- d. After digestion is complete, add an additional 1mL of 1:1 Ultrex HNO_3 and warm to dissolve any residue remaining from the evaporation process.
- e. Return sample to initial volume with D.I. Water.
- f. Matrix modifiers for each analyte added as needed by AS-40. See Ref. 7 for proper modifiers.
- g. The use of "Method of STD additions "Automated furnace procedures (ref. 5) follows the guidelines as set by EPA (ref.1)

3. A.A. Flame: Total Recoverable Metals

- a. Pour 50 mL of sample into a 250 mL Erlenmyer flask.
- b. Add 2.5 mL of 1:1 Ultrex HCl to each flask. The "Flame" acid matrix is now 0.5% HNO_3 and 5% 1:1 HCl .
- c. Digest sample to less than 1/2 the initial volume under a hood on a 400°C hot plate.
- d. Filter and return sample to original volume with D.I. Water.
- e. Add Matrix modifiers as needed, after cooling:
 - 1) Ca & Mg require addition of 1.0 mL La Cl_3 per 10 mL sample prior to analysis
 - 2) Al and Ba require 2mL of 10% KCl per 100 mL sample be added to sample prior to analysis

4. A.A. Graphite Furnace: Total Recoverable Metals

- a. Pour 30mL of sample into a 50mL Erlenmeyer flask.
- b. Add 0.5mL of 30% hydrogen peroxide
Note: Avoid the use of halide acids in all graphite furnace preparation.
- c. Digest to less than 1/2 the initial volume
- d. Filter and return sample to initial volume with D.I. Water.
- e. Matrix Modifiers for each analyte added as needed by AS-40. See Ref. 7 for proper modifier.
- f. The use of "Methods of STD additions" automated for furnace procedures follows the guidelines as set by Ref. 1, Metals, 8.1-8.5.

5. Cold Vapor: Hg only. (Perkin Elmer, Coleman MAS-50 instrument)

- a. Pour 100 mL sample into a BOD bottle (300mL) reserved for Hg only.
- b. Add 5mL concentrated Ultrex H_2SO_4 and 2.5 mL concentrated Ultrex HNO_3 .
- c. Add 15mL of 5% (w/v) KMnO_4 . If color fades, add 15mL more.

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- d. Add 8mL of 5% (w/v) potassium persulfate. Heat for two hours in a covered circulating water bath with the circulator on, dial set at 8.3, and the water level up to the water line of the samples. The water must be cool at the start.
- e. Remove the covering for the mercury analyzer vent
- f. Two hours before use, turn on the power switch of the Coleman MAS-50 instrument also turn on the pump switch located on the back of the instrument.
- g. Cool, add 6mL of 12% (w/v) Na Cl-hydroxylamine HCl solution to reduce excess KMnO_4 .
- h. Instrument adjustment
 - a. Push the meter switch to % T (middle setting)
 - b. With the shutter lever in the open position, use the 100% T knob to move the needle to 100 on the black dial.
 - c. With the shutter lever in the closed position, use the 0% T knob to move the needle to 0 on the black dial.
 - d. Push the meter switch to X5 (bottom position).
 - e. With the shutter lever in the open position, once again use the 100% T knob to move the needle to 100 on the black dial
 - f. Push the meter to X1 (top position). Read samples with meter in this position.
- i. Add 5mL of 10% (w/v) Stannous Chloride. (Shake the stannous chloride before using each time).
- j. Immediately connect the bottle to the aeration apparatus. Aerate and determine concentration of Hg which is proportional to the peak absorbance.

D. Instrumental Procedure - Ref. 7.

E. Data Handling Procedures:

1. Accuracy - Computerized
 - a. Mean & std. dev. control charts for Q.C. Standards.
 - b. % Recovery & std. dev. control charts for Q.C. Spikes.
2. Precision - Duplicates and Standard Curve, Computerized.
3. Data Recording Procedures:
 - a. Results recorded from graph or printer to bench log.
 - b. Results recorded from bench log to computer.
 - c. Samples and Q.C. results handled identically.

F. Quality Control:

1. Standards and % Recovery Standards.
 - a. Q.C. standards and spikes of samples for % recovery are made from a mixed substandard as indicated on chart. (See Figure 1

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STANDARD METHOD FOR DETERMINATION OF: Metals

- b. Quality control standard solutions contain the proper acid matrix as previously cited for either flame or furnace analysis. (See Section C)
- c. Working standards are prepared daily and contain proper acid matrix and modifiers as previously cited. (See Section C).
- d. Class A volumetric flasks and pipettes are used in all standard and spike preparation

2. Duplicates:

- 1. One duplicate analyzed for each 23 samples as 15th sample of run.
- 2. Duplicate should be randomly chosen.

3. Blanks:

- 1. Standard calibration blanks are prepared daily along with the standards to establish baseline or printer display zero.
- 2. Method or Digest blanks are processed along with samples as previously cited. (See Section C).

G. Glassware Washing:

All glassware is soaked in 1% Liqui-Nox and Water for 24 hours, rinsed with hot water, soaked for 24 hours in polyethylene tubs containing 1:1 HNO₃, manually rinsed in hot tap water and finally rinsed in D.I. Water.

H. Atomic Absorption Spectroscopy - Perkin - Elmer 272
Flame Analysis:

- 1. Turn on vent, power switch and compressor assuring pump and filter valves are closed on compressor.
 - a. Compressor is located in basement storage Room 10. Should be checked every Friday for Water build up, and drained as necessary.
 - b. Filters located on side of cabinet below Perkin-Elmer 272 should be checked regularly for brittleness and build-up of particulates. These are changed every 6 months regardless of condition and sooner if necessary.
 - c. Remove and clean burner head daily with D.I. Water.
 - d. Oxidant flowmeter (air) should read 50 units. (See "272" manual fig 7.4 for 4 min.)
- 2. Put analyte lamp(s) in mount (s) and with signal switch set on lamp, set specified current energy per lamp per channel. (i.e. lamp 1, copper=25 amp - lamp 2, iron=30 amp).
- 3. With signal switch on ABS, set proper wavelength and slit for analyte.
- 4. Set gain at 20.

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5. Align lamp to optimize lamp energy by:
 - a. Adjusting the two knobs on the lamp mount.
 - b. Adjusting burner height using horizontal & vertical knobs on burner mount so that lamp beam "sits on burner and is centered over burner slit."
6. Allow lamp 15-30 minutes to warm up.
7. Turn on acetelyne, ignite flame, aspirate D.I. water blank and allow lamp energy meter to stabilize (approximately 15 minutes time with gain set at 40).
8. After 15 minutes, cease aspiration, shut off fuel and recheck wavelength and alignment process.
9. Re-ignite flame, set gain at 40 and check stability.
10. When satisfied with all steps above, aspirate analyte standard. (See Ref 7 for sensitivity check).
11. When sensitivity check is satisfactory, proceed with standardization.
12. Turn signal switch to conc mode, press autozero calibrate instrument:
 - a. Aspirate high standard as instrument S1.
 - b. If linearity cannot be achieved use middle standard as S1 and high standard as S2 as directed in instrument instructions.
13. Calibration standards for each element and how to prepare them are in Ref. 7.
14. Analyze samples and standards periodically to check linearity and calibration.
15. If lamp energy needle drifts out of green area, repeat steps 8&9.
16. To shut down A.A., reverse procedure
 - a. Drain compressor pump and filter daily
17. Consult Perkin-Elmer 272 AAS Manual for additional information.

I. Atomic Absorption Spectroscopy - Perkin Elmer
560 With HGA 500. Graphite Furnace Analysis:

1. Turn on vent and power switches for "560" EDL Power Supply Records, Autosampler, and Furnace Programmer.
2. Clean quartz windows in furnace daily with ethanol. Check graphite tube and contact rings, replacing if necessary.
3. Turn on Argon.
4. Turn on water valve
5. Put on analyte lamp and mount in AA, setting specified lamp current on EPL power supply (or AA-lamp signal knob if using Hollow Cathode lamp.) Warm up EDL 10 min. and HC 15-30 min.
6. With signal knob in set-up:
 - a. Set proper wavelength and slit for analyte.
 - b. Align lamp to optimize lamp energy.
 - c. Maintain lamp energy at 40.
 - d. Set background corrector knob at AA.
(Note 1:) If background corrector is necessary set knob in AA-BG position after lamp energy above has stabilized and allow and additional 15 minutes for warm-up.
7. Turn recorder to "amp" to warm-up.

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8. Inspect Auto sampler (AS-40) capillary tube to insure that there are no air breaks. Inspect wash reservoir, fill if necessary.
9. Program furnace for respective analyte lamp according to Ref. 7 guidelines.
10. Adjust max power/max temp dial as needed if internal gas flow is zero during max power atomization.
11. Run conditioning program (See Perkin Elmer HGA-500 manual) for new tubes.
12. Reinspect all energy levels for optimum level and stability DO NOT exceed manufacturer's designated lamp current level.
13. When satisfied with above, turn signal knob to ABS and set recorder range and integration time according to program.
14. Standardize AA for each metal. Proper S1-S2-S3 settings for each metal are in Ref. 7.
15. Analyze samples and standards periodically to check linearity and calibration.
16. To shut down AA, reverse start-up procedures.
17. Consult Perkin-Elmer "560" AAS Manual and HGA 500 Graphite Furnace Manual for additional information.

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STANDARD METHOD FOR DETERMINATION OF: Metals

<u>Item Number</u>	<u>Name Of Metal</u>	<u>Symbol For Metal</u>	<u>Computer Test</u>	<u>Technique Used</u>
1	Aluminum	Al	40	AA Flame
2	Barium	Ba	42	" "
3	Beryllium	Be		" "
4	Calcium	Ca	44	" "
5	Chromium	Cr	45	" "
6	Copper	Cu	46	" "
7	Iron	Fe	47	" "
8	Magnesium	Mg	49	" "
9	Manganese	Mn	84	" "
10	Nickel	Ni	51	" "
11	Potassium	K	52	" "
12	Sodium	Na	55	" "
13	Thallium	Tl		" "
14	Zinc	Zn	57	" "
15	Aluminum	Al	40	AA Furnace
16	Arsenic	As	41	" "
17	Cadmium	Cd	43	" "
18	Chromium	Cr	45	" "
19	Copper	Cu	46	" "
20	Lead	Pb	48	" "
21	Selenium	Se	53	" "
22	Silver	Ag	54	" "
23	Antimony	Sb	200	" "
24	Vanadium	V	202	" "
25	Molybdenum	Mo	201	" "
26	Mercury	Hg	50	Cold Vapor

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STATE OF N.H. WATER POLLUTION CONTROL LABORATORY
STANDARD METHOD FOR DETERMINATION OF: pH Value

References:

- 1 EPA Manual, March 1979, Revised March, 1983, Method 150.
- 2 1985 Annual Book of ASTM Standards Section 11, Water and Environmental Technology.
- 3 Standard Methods 16th edition, 1985, part 423, p 429-437.
- 4 Beckman (Altex) Instructions 015-556363, pp 11-13 (1981).

TECHNIQUE USED: Electrometric.

A. Sampling Methodology:

1. Preservative: 4°C, first chemical test performed on sample.
(after bacteria)
2. Holding Time: Analyze immediately.
3. Required Volume: 25 mL:
4. Container Type: Polyolefin or glass, plastic preferred.

B. Instrument Set-Up and Run:

1. Check KCl filling solution in electrode for precipitate and level of solutions and presence of crystals on outside of probe. Remove clothespin from the fill hole, when electrode is in use. If precipitate or crystals are present, change the filling solution.
2. Standardize and calibrate meter as follows: (NOTE 2) (NOTE 3).
 - a. Immerse electrode in buffer solution of pH 4.0 (NOTE 1) with stirring bar in 30 mL plastic beaker.
 - b. Push CAL button. When (arrow) appears take off 4.0 solution. Rinse and blot electrode. Place in pH 10.0 buffer solution and push CAL button again. When (arrow) appears remove 10.0 solution, rinse electrode and measure pH of 4.0 solution again. If not on correct reading, repeat the above procedure. If still off, make new solutions and start over.
3. To measure samples and Q.C. standard, pour sample into 30 mL plastic beaker with a small stirring bar (0.75"), place on magnetic stirrer, and stir slowly with electrode immersed in sample. Switch meter to pH mode and record reading when (eye symbol) and (arrow) show on meter.
 - a. Do not generate a vortex or air bubbles when stirring.
 - b. Use a separate stirring bar for each sample.
4. When finished measuring samples, keep electrode immersed in deionized water and leave on pH, clear at end of day only.

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STANDARD METHOD FOR DETERMINATION OF: pH Value

TECHNIQUE USED: Electrometric

NOTE 1: Use pHdrion certified capsules made up in 100 mL of deionized water.

(pH 4.00 VWR Cat. No. 34175-129, 10.00 VWR Cat. No. 34175-399)

NOTE 2: Once the electrode is set up and placed into its holder, take care that it is disturbed as little as possible during the analysis. The electrode should be moved from sample to sample in the following manner.

- a. Lift the sample cup slightly off the stirrer being careful not to hit the electrode.
- b. Carefully slide the stirrer back and away from the sample cup and the electrode.
- c. Drop the sample cup directly down then away from the electrode.
- d. Rinse the electrode well with DI water.
- e. Place the next sample cup under the electrode and raise it up enough so that the stirrer can be slid back underneath the cup and electrode.
- f. Continue measuring subsequent samples and standards as in 8.3.

NOTE 3: Fisher Combination Electrode, Cat. No. 13-369-80 w/Fisher 13-640-155 Adaptor, Beckman "Altex 060" Meter, VWR 34101-417.

C. Data Handling Procedures:

1. Accuracy

a. Control charts

- 1) \bar{x} for Q.C. standards.

2. Precision

a. Duplicates, (\bar{R}) Chart

3. Recording Procedures:

Enter all sample and Q.C. data into the computer.

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STANDARD METHOD FOR DETERMINATION OF: pH Value

TECHNIQUE USED: Electrometric

D. Quality Control - 20%:

1. Stock Solutions - prepare buffer solutions of 10.0 pH and 4.0 pH by dissolving pHdrion buffer capsules in 100 mL of deionized water. Make new each week. Keep capsule in desiccator.
2. Q.C. Standard - Altex/Beckman 7.00 buffer, VWR 34181-303. Use as received. Run one every 10 samples.
3. Duplicates - Run one duplicate for every 10 samples.
4. Repeat above format for each additional set of 10 samples to assure 20% quality control.

CND/pdl
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STATE OF N.H. WATER POLLUTION CONTROL LABORATORY
STANDARD METHOD FOR DETERMINATION OF: Conductivity

Reference:

- 1 EPA Manual, March 1979, Revised March, 1983, Method 120.1.
- 2 Standard Methods for the Examination of Water and Wastewater
16th edition, 1985, Part 205, p 76-80

TECHNIQUE USED: Conductivity Bridge and Cell, mhos/cm at 25°C

A. Sampling Methodology:

1. Preservative: 4°C
2. Holding Time : 28 days
3. Required Volume: 100 mL
4. Container Type: polyethylene or glass

B. Instrument Set-Up: Beckman Conductivity Bridge Model RC-16C instructions

1. Set power toggle switch to 85 Hz
 - (a) Set conductance scale to balance knob (blue mhos) to 1000
 - (b) Set multiplier scale to 1
 - (c) Turn sensitivity knob to approximately midrange of null meter
2. Attach conductivity probe (Beckman industria) PT# 265-10758627) to cell posts #1 & #2
3. Pour 100 mL of sample/standard into short & glass cylinder.
4. Immerse probe in sample/standard to completely cover the hole on the side of the probe. Switch multiplier knob for maximum deflection towards zero on null meter.
5. Once the null meter zeros (a) turn balance knob clockwise until the null meter deflects positively. Note the number of divisions deflected on the umhos scale. Zero the null meter again with the balance knob (b) turn the balance wheel counterclockwise until the null meter deflects positively. Note the number of units of deflection on the umhos scale. Add together the number of units of deflection in (a) & (b). Coordinate dialing of balance and sensitivity knobs until the above sum is less than 5 divisions. The sensitivity knob is generally increased to achieve the 5 division minimum, deflection requirement.
6. After the total 5 division requirement is met, turn the balance knob so the null meter is at zero. Record umhos scale reading (blue scale)
7. Record scale multiplier factor
8. Check temperature of sample with digital thermometer set on °C.
9. Record thermometer and temperature factor readings found on chart in drawer underneath meter.

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STATE OF N.H. WATER POLLUTION CONTROL LABORATORY
STANDARD METHOD FOR DETERMINATION OF: Conductivity

NOTES:

1. Check conductivity of DI Water every day before running samples. Let DI Water run for 2 minutes then collect 100mL into a clean graduated cylinder. Record in bench log as DI Blank. Results should be 1.00 or less. If results are higher than 1.00 report to area supervisor.
2. Rinse cell with deionized water between samples.
3. Recording Procedures
 - a. Record reading (umhos) = B
 - b. Record sample temperature, °C.
 - c. Determine factor = A by multiplying together:
 1. Scale multiplier factor - A
 2. Temperature factor-determined from 25 °C equivalent values chart.
 3. Probe factor = 1.00 (This must be determined for each probe).
 - d. Multiply A X B to obtain umhos/cm.
 - e. Record results in bench log and in computer.
 - f. Record results in bench log and in QC File in computer.
 - g. Record results on computer.

2. *Factors for Converting Specific Conductance of Water to Equivalent Values at 25°C. (Std. Methods 13th Ed. p 324)

<u>Temp (°C)</u>	<u>Factor</u>	<u>Temp (°C)</u>	<u>Factor</u>	<u>Temp (°C)</u>	<u>Factor</u>
5	1.58	15	1.23	25	1.00
6	1.54	16	1.21	26	0.97
7	1.50	17	1.18	27	0.95
8	1.46	18	1.16	28	0.93
9	1.43	19	1.13	29	0.92

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STANDARD METHOD FOR DETERMINATION OF: Conductivity

<u>Temp (°C)</u>	<u>Factor</u>	<u>Temp (°C)</u>	<u>Factor</u>	<u>Temp (°C)</u>	<u>Factor</u>
10	1.40	20	1.11	30	0.90
11	1.36	21	1.08		
12	1.32	22	1.06		
13	1.29	23	1.04		
14	1.26	24	1.02		

*Note: Factors extrapolated from curve (expanded) in "Std. Methods"

COMMON CONDUCTIVITIES OF N.H.

less than 0.5 - 5.0 : Pure Water	80 - 200 : Private wells
3.0 - 20.0 : Rain or Snow	200 - 600 : Contaminated wells
60 - 90 : Oligotrophic lakes and clean rivers	190 - 1,500 : Treatment plant effluents
100 - 200 : Eutrophic lakes; larger rivers	1,000 - 10,000 : Groundwater leachates
	9,000 and greater : Saline waters

F. Quality Control - 20%:

1. QC Standard: Dissolve 7.4555 g of Potassium Chloride (KCl) in deionized water and dilute to 1 liter for a 0.1M KCl solution. Dilute 10 mL of 0.1 M KCl solution to 1 liter in deionized water for a QC standard of 146.93 mhos/cm specific conductivity.

a. Run as 5th, 15th, 25th samples, etc..

2. Duplicates: Run duplicates - once every ten samples. Duplicate range is calculated by subtracting the difference of the final readings and left justifying the decimal.

3. Check standardization of instrument every 6 months with the following KCl standards: (should be done on a regular basis).

<u>Concentration (M)</u>	<u>Conductivity (mhos/cm)</u>
0.0001	14.94
0.0005	73.90
0.001	147.0
0.005	717.8
0.01	1,413
0.02	2,767
0.05	6,668
0.1	12,900
0.2	25,820

STATE OF N.H. WATER POLLUTION CONTROL LABORATORY
STANDARD METHOD FOR DETERMINATION OF: Volatile Organic Compounds

References:

1. Federal Register; October 26, 1984; Methods 601-602, pp. 43261-43280

TECHNIQUE: Purge Trap Gas Chromatography (Hewlett-Packard 5880 A-FIO)

A. SAMPLING METHODOLOGY:

1. Preservation: 100 uL $HgCl_2$ (4.3 mg/mL conc.); 4°C
2. Holding Time: 14 days
3. Required Volume: 40 mL
4. Container type: 40mL precleaned vial with teflon screw cap.

B. INSTRUMENT SET-UP and RUN:

1. G.C. conditions:

- | | |
|-----------------------------|---------------|
| a. Initial temperature | 70° |
| b. Initial time | 4.00 minutes |
| c. Level 1 program | |
| 1) Program rate | 10°C/minutes |
| 2) Final Temperature | 220°C |
| 3) Final Time | 15.00 minutes |
| d. FID Detector temperature | 250°C |
| e. Injector temperature | 150°C |
| f. Chart Speed | 0.3cm/min. |
| g. Peak Width | 0.1 |

2. Column type: 1.0% SP-1000 or 60/80 Carbopack B

3. Trap: The packing in the trap consists of 8 cm #15 silica gel, 15 cm GC Tenax, 1 cm 3% OV-1, and is plugged at each end with glass wool.

C. AUTOMATIC PURGE TRAP CONDITIONS:

1. Temperature Functions:

- | | |
|----------------|------------|
| a. Purge Time | 11 minutes |
| b. Desorb Time | 4 minutes |
| c. Bake Time | 7 minutes |

D. MECHANICAL OPERATION:

1. Switch on lower auto-sampling unit to AUTO mode.
2. Turn first cycle light to the position of the first sample
3. Purge trap should be baked out for about 10 minutes every day.

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4. If heavily contaminated samples were run the day before, the purge cells should be baked out in the morning to prevent carry over (5min/trap.)
5. Every two weeks, or as conditions dictate, the glass chambers should be removed and immersed in 50% HNO₃ for 24 hours. Prior to reinstallation the chamber should be rinsed well with DI water.

E. REAGENTS:

1. Blank Water
 - a. Water from a Sybron/Barnstead megohm-cm #82770 Water Purifying System is boiled for 15 minutes.
 - b. Allow to come to room temperature
 - c. Prepare new blank water if blank run has interferences.
2. Stock Standard
 - a. Prepare stock standards in volumes of 100 mL
 - b. Transfer to amber bottle and store at 4°C
 - c. Shelf life: 6 months
3. Intermediate Standard
 - a. Usually a 1:50 dilution of the stock standard. The dilution should be such that the final dilution will appropriate the analytical averages of the system.
 - b. This standard is given a lot number, sealed in glass vials, and stored at 0°C
 - c. Dilution is used for about 1 week to make up working standards
4. Working Standards
 - a. 0.002 mL to 5.0mL dilutions of intermediate standard. This dilution will yield levels of 20-30 ug/L of the volatile organic compounds of interest
 - b. Other working dilutions may be necessary depending on the group of standards being analyzed
5. Purge Trap Calibration Standards

<u>Compound</u>	<u>(g/ml)</u> <u>density</u>	<u>MEOH</u> <u>Vol to 50mL</u>	<u>Stock</u> <u>Std.</u> <u>(fmq/L)</u>	<u>Inter.</u> <u>Std.</u> <u>(1 to 50)</u>	<u>Workin</u> <u>Std.</u> <u>(2 uL t</u>
MeCl ₂	1.3266	250 uL	6633	132.66	53.0
1,1 diChloroethylene	1.213	200 uL	4872	97.44	38.9
t - 1,2-diChloroethylen	1.2565	150 uL	3769.5	75.39	30.1
1,1-diChloroethane	1.1757	200 uL	4702.8	94.056	37.6
Chloroform	1.4832	150 uL	4449.6	88.99	35.6
1,2 diChloroethane	1.2351	150 uL	3705.3	77.106	29.64

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<u>Compound</u>	<u>(g/ml)</u> <u>density</u>	<u>MEOH</u> <u>Vol to 50mL</u>	<u>Stock</u> <u>Std.</u> <u>(fmq/L)</u>	<u>Inter.</u> <u>Std.</u> <u>(1 to 50)</u>	<u>Worki</u> <u>Std</u> <u>(2 uL t</u>
1,1,1 Trichloroethane	1.3390	150 uL	4017	80.34	32.1
Trichloroethylene	1.4642	150 uL	4392.6	87.85	35.1
Toluene	0.8669	250 uL	4334.5	86.69	34.6
Chlorobenzene	1.1058	200 uL	4423.2	88.46	35.3
Ethylbenzene	0.8670	250 uL	4335	86.70	34.6
M-xylene	0.8642	250 uL	4321	86.42	34.5
O-xylene	0.8802	125 uL	2205.5	44.01	17.6
P-xylene	0.8611	125 uL	2152.75	43.055	17.2
Benzene	0.8765	250 uL	4382.5	87.65	35.0
Tetrachloroethylene	1.6227	150 uL	4868.1	97.36	38.9

Purge Trap Internal Standard:

Fluorobenzene	1.0225	2.5 uL	51.125	-----	20.45
---------------	--------	--------	--------	-------	-------

6. Internal Standard

- 20.0 ug/L flurobenze
- The internal standards are prepared monthly, sealed in ampules and stored at 0°C
- One ampule is used until signs of contamination appear, usually 1 week

7. HgCl₂

- Dissolve 2.15g HgCl₂ reagent grade into 500 mL of organically pure water (blank water) and store in amber bottle
- Solution is made once a month or as indicated

F. SAMPLE TYPE:

- This system was developed to handle the SDWA samples.
- Private samples are usually done by GC/MS, but may be done on this system when sample load on GC/MC is taxing

G. DATA HANDLING:

- Data Recording Procedures:
 - The program KEN* on the lab computer will calculate the new response factors.

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- b. The program KEN** on the lab computer will calculate the percent difference in the response factors.
- c. The response factors and the percent deviation should be recorded in the GC - HP 5880A notebook.
- d. The integration of the data is done on the 5880A integrator. This is an internal standard method.
- e. The data is reviewed by the supervisor.
- f. The data is then entered into the general laboratory computer for dissemination.

2. Accuracy

- a. % Recovery of QC spike - recorded in the QC - GC - HP 5880A notebook
- b. Run an EPA QC check sample once every month to ensure that the integration system is in control. Record results in the GC - 5880A notebook

H. QUALITY CONTROL

1. Data Review

- a. The analyst should take special care that the compound of interest has not exceeded the range of linearity of the instrument.
- b. If the sample has exceeded the linear range, a dilution should be made and run. If it is not possible to make a dilution, report values of greater than for the compounds involved, and request a resample.
- c. Minimum detection limits for each compound. (See run of August 5, 1986 for actual values received on each of 9 runs).

Compound	MDL
1,1 - Dichlorobenzene	4.38
1,1, Dichloroethane	2.39
t - 1,1 - Dichloroethylene	3.07
CHCl ₃	5.67
1,2 - Dichloroethane	2.54
1,1,1 - Trichloroethane	2.86
Trichloroethylene	2.83
Benzene	2.41
Tetrachloroethene	3.10
Toluene	2.44
Chlorobenzene	2.56
Ethylbenzene	2.96
m-X ylene	2.94
o-X ylene, p-X ylene	2.76

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Note: The 40mL sample vials should be cleaned; they may be revised by the pesticides and radiological departments. The analyst processing the samples is responsible for cleaning and storing his/her vials.

CND/pdl
0311C

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STANDARD METHOD FOR DETERMINATION OF: Volatile Organic Compounds
Federal Register, July 1, 1982, Method 624, (624-1, 624-11).

A. Sampling Methodology:

1. Preservative: 100 microliters of HgCl_2 (4.3 mg/ml concentration) and storage at 4 C.
2. Holding Time: 14 days
3. Required Volume: 40 mL
4. Container Type: 40 mL precleaned vial with teflon screw cap.

B. Techniques:

1. Gas Chromatography/Mass Spectrometry - with 10 chamber automatic purge trap.

C. Instrument Set-Up and Run:

1. GC/MS Conditions

a. Gas chromatograph conditions:

Initial Temp	700 C
Hold Time	12.5 Min.
Final Temp	2200 C
Final Time	300 Min.
Ramp	15 C/Min
Inj. Temp	125 C
TCD Temp	240 C
AUX Temp	240 C
Chart Speed	0.01
Zero	10.0
FID Signal	+B
Vlv/Ext. 1	time 0
Vlv/Ext. -1	time 0.02

b. Column Type: 1.0% SP-1000 on 60/80 carbopack B.

c. Trap: The packing in the trap consists of 8 cm #15 silicon gel, 15 cm GC Tenax, 1 cm 3% OV-1, and is plugged at each end with glass wool.

d. Mass Spectrometer conditions:

Ion Source Temp	240 C
Low Mass	45
High Mass	220
A/D	3
Threshold	50
High Voltage	as required

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2. Automatic purge trap condition:

a. Temperature functions

purge time 11 minutes
disorb time 4 minutes
bake time 7 minutes

b. Mechanical operation:

1. Switch on lower auto-sampling unit to AUTO mode.
2. Turn first cycle light to the position of the first sample.
3. Purge cells should be baked out every morning to prevent carry over (5 minutes/trap).
4. Every two weeks, or as conditions dictate, the glass chambers should be removed and immersed in 50% HNO₃ for 24 hours. Prior to reinstallation the chambers should be rinsed well with D.I. water.

D. Reagents:

1. Blank Water

- a. Water from a Sybron/Barnstead megohm-cm #82770 water purifying system is boiled for 15 minutes.
- b. Allow to come to room temperature
- c. Prepare new blank water if a blank is run that contains interferences.

2. Standards

a. Stock standards

- (a) Prepare stock standards in volumes of 100 mL.
- (b) Transfer to amber bottles and store at 4°C. The shelf life for these is 6 months.
- (c) In the case of chloroethane, chloromethane, bromomethane and vinyl chloride; transfer to teflon-sealed screw cap amber bottles and store at -20°C, away from light. These standards are to be made up weekly.
- (d) Intermediate standard
 1. Usually a 1:50 dilution of the stock standard. The dilution should be such that the final dilution will appropriate the analytical averages of the system.
 2. This standard is given a lot number, sealed in glass vials, and stored at 4 C.
 3. Dilution is used for about 1 month to make working standards.

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(e) Working standards

1. 0.004 mL:5.0 mL dilution of intermediate standard.
This dilution will yield levels of 20-30 microgram/L of the volatile organic compounds of interest.
2. Other working dilutions may be necessary depending on the group of samples being analyzed.

(f) Internal standard

1. 20.0 micrograms/L fluorobenzene standard
2. 25 micrograms/L p-bromo-fluorobenzene (this compound is used as the tuning standard).
3. The internal standards are prepared monthly, sealed in ampules and stored in freezer.
4. One ampule is used until signs of contamination appear, usually one week.

(g) Preservative

- a. Mercuric Chloride Powder - Fisher Scientific Company (reagent grade)
- b. Dissolve 2.15 g into 500 mL of organically pure water (blank water) and store in amber bottle.
- c. Solution made once a month, or as indicated.

E. Data Handling:

1. Accuracy

- a. % Recovery of Q.C. spike - recorded in the Q.C. - GC/MS notebook.
- b. Run an EPA QC check sample once every 20 runs, or 5%, to ensure that the integration system is in control. Record results in the GC/MS QC logbook.

2. Precision

- a. Duplicates
- b. % difference in response factors - on a daily basis.
- c. GC/MS calibration standard - bromofluorobenzene on a daily basis.

3. Data Recording Procedures

- a. The integration program (m) is used to integrate the data.
(Hewlett Packard 1000, E series, attached to the GC/MS)
- b. Hardcopies of the integration are printed by the Hewlett Packard Printer 9876A.
- c. The data is then reviewed by the supervisor.
- d. The data is then entered into the general laboratory computer for dissemination (Hewlett Packard 1000, E series).

F. Quality Control - 20%:

1. Data Review

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- a) The analyst should take special care to ensure the compound of interest has not exceeded the maximum peak area count allowed by a 16-bit computer (32767 counts).
- b) If the area count has exceeded the 32767, a secondary ion, of lesser abundance, should be selected to be targeted by the integration program. If this is not possible, then the run should be repeated on dilution, or the data report must be prefaced with a "greater than" for the reported concentration.

2. Duplicates

- a. 20% of all samples are duplicates and the results of these analyses must be recorded appropriately for quality control purposes.
- b. Once a week the analyst will spike one of the duplicate samples with an EPA surrogate standard solution to monitor the recoveries. These results should be recorded in the mass spectrometer log book.

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STANDARD METHOD FOR DETERMINATION OF: Cyanide

References:

1. EPA Manual, Method 335.2, 1-9; March 1979, Revised March 1983.
2. "STANDARD METHODS", 16th ed, 1985, Part 412B, pp 334-338.

TECHNIQUE USED: Distillation; Spectrophotometric

A. Sampling Methodology

1. Preservative: 4°C; 1.0 g ascorbic acid, 0.5g (12-20) Na OH pellets. At the time of collection the pH must be between 11-12.
2. Holding Time: 24 hours
3. Required Volume: 1 Liter (Note 1)
4. Container: polyethylene

B. Apparatus

1. Wheaton Cyanide Distillation Apparatus (See diagram A)
2. Vacuum source
3. Glas-Cal 380 watts 115 volts heating mantles with variable transformers
4. Beckman Du-7 or B & L 710 Spectrophotometer set at 580.5 nm with a 2.0 cm cuvette
5. Fume hood with very good draw

C. Sample Preparation

1. Prepare a standard solution of KCN in the 10 - 800 ug CN/L range.
2. Assemble three sets of distillation apparatus under the hood. (See diagram A)
 - a. Pour 250 mL of sample into a 1 L boiling flask. At the same time, set up a standard and a quality control sample. If the sample is known or suspected to be in the high range use a smaller volume. Record volume used in column B of the worksheet.
 - b. Pour 50 mL of 1.25 N NaOH into each absorbing tube.
 - c. Check that all connections are tight and clamp each connection with a blue blue joint clip. (See diagram A)
 - d. Start stirrers and water flowing, keeping the condensers full.
 - e. Start vacuum source with all needle valves closed tightly. Slowly adjust the vacuum until the gauge reads 4-5 units.

NOTE 1. A 500 mL sample must be collected at the same time and tested for sulfide prior to cyanide analysis. Sulfide constitutes a negative interference with cyanide analysis and must be removed by precipitation with lead carbonate. Add Pb (CO₃)₂ until a drop of sample no longer darkens acidified lead acetate test paper. Decant sample to remove precipitate before continuing.

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- f. Slowly adjust needed valves until a flow rate of two bubbles/second is entering the distillation flask and the bubbles in the absorbing tube are approximately 1 inch from the top of the tube.
 - g. Add 2 g sulfamic acid to each distillation flask and mix for 3 minutes. This reduces any interference from NO_2/NO_3 .
 - h. Add 50 mL 18 N H_2SO_4 to each of 3 100 mL or larger separatory funnels. Insert one separatory funnel into each inlet tube. Slowly open stopcocks until a slow even stream enters the distillation flask without interrupting the air flow. Allow funnel to drain. Rinse with DI water and check to be sure solution is now acidic. If not, add additional H_2SO_4 solution. Allow to mix for 3 minutes.
 - i. Add 20 mL magnesium chloride solution to each separatory funnel, allowing it to enter the flask. Rinse with DI water.
 - j. Start heating units and allow to reflux for 1 1/2 hours.
 - k. Turn off heating units. Allow air flow to continue for 1/2 to 1 hour.
 - l. Turn off vacuum pump.
 - m. Remove absorbers. Force out any remaining solution from bubbler into absorbing tube with air bulb. Empty absorbing tube into a 250 mL volumetric flask. Rinse bubbler into absorbing tube and tube into flask 3 times with DI water. Bring to volume using DI water.
3. Preparation of standard solutions:
 Use an appropriate volume of the 10 mg CN/L KCN working solution; 50 mL 1.25 N NaOH; dilute to 250 mL with DI water.
 (Use 250 mL volumetric flasks)

<u>mL KCN working solution</u> <u>1 mL = 10 ug CN</u>	<u>Conc ug CN</u> <u>per 250 mL</u>	<u>For samples known to be in</u> <u>the 0-50 ug/L range</u>
0	Blank	0
1.0	10	3
2.0	20	5
5.0	50	10
10.0	100	20
15.0	150	50
20.0	200	100
25.0	250	

Note 2. If sample may have a value greater than 1 mg/L, use 25 mL of sample and 25 mL of 0.25 N sodium hydroxide solution or an appropriate portion of each to equal 50 mL. Remember to record the amount of sample used in column C of the worksheet.

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STANDARD METHOD FOR DETERMINATION OF: Cyanide

4. Put 50 mL of sample or standard in a 100 mL volumetric flask. (See Note 2) If only one sample is being run, choose one of the three distillates to be run in duplicate. Record volume of sample used in column C of the worksheet.
5. Add 15.0 mL of sodium phosphate solution to each flask and shake.
6. Add 2.0 mL chloramine T to each flask; shake. Check for excess Cl with KI starch paper. If necessary, add additional chloramine T. Wait for 2 minutes.
7. Add 5.0 mL of pyridine - barbituric acid solution and mix. Bring to volume using DI water and mix. Allow 8 minutes for color development. Read within 1/2 hour.

D. Instrument Calibration and Sample Determination

1. Turn on spectrophotometer at least 20 minutes in advance.

For B & L Spectronic 710

2. a. Set wavelength to 580 nm. Tungsten lamp mode switch to "absorbance". Using the "zero adjust knob", adjust to ".000" using the method blank in a 2.0 cm* cylindrical cuvette in the inner cuvette holder. Keep in place.
b. Fill a second 2.0 cm* cuvette with method blank. Place in outer cuvette holder and read. If reading is greater than .005 exchange the places of the two cuvettes and repeat steps a and b. Record reading on worksheet under absorbance on the blank line.
c. Remove outer cuvette. Empty. Rinse with next sample to be read.
3. Read all standards and samples in the outer cuvette holder. Always check the zero as in 2a. above to be sure that no instrument drift has taken place. Record absorbance reading on worksheet in the appropriate space.
4. After all samples have been read, rinse cuvette with a dilute bleach solution. Rinse three times with hot tap water. Rinse three times with DI water. Fill with DI water and store.
5. Generate a standard curve of the undigested standards using the computers CURVE program. Make a copy of the plot and tape it to the back of the worksheet. Generate data and retrieve hard copy labeling it as follows:

Cyanide	Date	Analyst	Vol	P	No
---------	------	---------	-----	---	----

Tape to the back of worksheet after filling in concentrations in Column A of worksheet.

*Note: For low level samples, use the 10 cm cuvette if possible

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STANDARD METHOD FOR DETERMINATION OF: Cyanide

For Beckman Du-7

2. Using the (SEL) button, move the cursor to :
 - a. Single λ , screen should read #01
 - b. Function, screen should read (Abs)
 - c. Wavelength, enter 580.5
 - d. Standard, enter the mid range standard which is usually 100.0
3. Put in blank. Push start button. Put in standard. Hit run. At the top of the screen the factor should read 180-210. If not, something is wrong with the analysis. Check for error in your procedures.
4. Put in blank. Push run 3 times. It should read 0. Continue with standards and samples, doing 3 readings of each.
5. Print out report and save with CN worksheet.
6. Calculate CN concentration in the original sample using the equation concentration

$$(\text{ug CN/L}) = \frac{A \times 1000}{B} \times \frac{50}{C}$$

A= ug CN/mL off std curve
B= mL sample used
C= mL used for
colorimetric analysis

Record value in bench log in ug/L. Convert to mg/L and record on computer.

E. Preparation of Standard Solutions

1. KCN (1000 mg CN/L) stock:
Dissolve 0.251 g KCN and 0.2 g KOH in 50 mL of DI water. Dilute to 100 mL.
Holding time - 6 months.
2. KCN (10 mg CN/L) working solution:
Dilute 1 mL of KCN (1000 mg CN/L) stock to 100 mL with DI water.
(1 mL = 10 mg CN)
Holding time - 12 hours.
3. 1.25 N NaOH:
Dissolve 50 g NaOH pellets. Dilute to 1000 mL with DI water.
4. 18 N H₂SO₄:
Dilute 250 mL conc. H₂SO₄ to 500 mL with DI water.
5. Sodium Phosphate:
Dissolve 34.5 g sodium phosphate. Dilute to 250 mL with DI water.
Holding time - 1 month at 40°C.
6. Magnesium Chloride:
Dissolve 102 g magnesium chloride. Dilute to 200 mL with DI water.
Holding time - 6 months.
7. Chloramine T:
Dissolve 1 g chloramine T. Dilute to 100 mL with DI water.

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STANDARD METHOD FOR DETERMINATION OF: Cyanide

Holding time - 12 hours.

(See Note 3)

8. Pyridine-Barbituric acid color reagent:

Dissolve 6 g barbituric acid in small amount of DI water. Add 30 mL pyridine (spectrophotometric grade). Swirl well. Add 6 mL conc H Cl. Swirl until cool and homogeneous. Dilute to 100 mL with DI water. For more than 18 readings, increase amounts as follows: final volume - 250 mL; barbituric acid - 15 g; pyridine - 75 mL; and conc H Cl - 15 mL.

Holding time - 1 month.

9. Bleach solution:

A wash bucket and wash bottle of bleach solution (approximately 5% sodium hypochlorite) should be on hand at all times where CN is being used.

a. Wash bucket:

Dilute 50 mL bleach to standard size waste bucket with tap water.

b. Wash bottle:

Dilute 10 mL bleach to 500 mL with tap water.

F. Data Handling Procedures

1. Accuracy

a. Control chart % recovery for distilled standard.

b. EPA check vial must be within acceptable limits.

2. Precision

a. \bar{R} chart for duplicates.

3. Recording Procedure

a. Volume (mL) used in distillation = B

b. Reading off standard curve = A

c. Volume (mL) used in colormetric analysis = C

d. Absorbance units as read off spectrophotometer

e. Concentration in ug/L = X

$$X = \frac{A \times 1000 \times 50}{B \times C}$$

f. Record all of above on worksheet. Keep worksheet in lab file.

g. Record all Q.C. information on charts kept with bench log.

h. Record all samples, duplicates, and QC from worksheet into bench log.

Note 3. Chloramine T powder should be loose and white in color. If it is not, it has lost Cl and is no longer good.

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STANDARD METHOD FOR DETERMINATION OF: Cyanide

G. Quality Control

1. For 1-2 samples, 3 distillation setups are used - sample, known standard from KCN (10 mg CN/L) working solution, spike. One of the samples above should be used twice in the colorimetric analysis as a duplicate.
2. For 3 or more samples, 1 standard, 1 EPA check vial, or 1 spike, and 1 duplicate distillation should be run. A second duplicate as above may also be run.
3. If QC's are unacceptable, the site should be resampled and the analysis rerun. The original sample will be past the holding time.

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STANDARD METHOD FOR DETERMINATION OF: Cyanide

Cyanide Worksheet - Final Vol (mL)

Sample	<u>B</u> mL Used in Distillation	Absorbance (578 nm)	<u>A</u> Concentration Curve	<u>C</u> mL Final Vol	CN Concentration in Original Sample (ug/L)
Blank					
10					
20					
50					
100					
150					
200					

$$\text{Concentration CN in ug/L} = \frac{A \times 1000}{B} \times \frac{50}{C}$$

Run Date:

Analyst:

2456X
pdl

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STANDARD METHOD FOR DETERMINATION OF: Base/Neutrals & Acids
Federal Register, July 1, 1982 Edition, Method 625
Method 604

TECHNIQUE USED: GC/MS - Direct Injection

A. Sampling Methodology:

1. Preservative: Storage at 4° C.
2. Holding Time: 5 days before extraction, 30 days after extract.
3. Required Volume: 1000 mL
4. Container Type: Glass bottle with Teflon seal on cap.

B. Techniques:

1. A sample is first extracted for base/neutrals, then pH is lowered and the same sample is back extracted for the acid extractables.
2. All extracts are screened on a gas chromatograph.
3. Confirmation and quantitation is done by GC/MS (gas chromatography/mass spectrometry).

C. Sample Preparation:

1. Base/Neutrals Extractions
 - a. Pour 1000 mL of sample into a 2000 mL separatory funnel.
 - b. Adjust the pH of sample to 12 pH units if needed (use either 1:1 Sulfuric Acid or 10N NaOH as required).
 - c. Add internal standards, spikes and surrogates, for both the Base/Neutral extraction, and the acid extraction, at the same time. (The internal standard for the Base/Neutral extraction is Hexamethylbenzene - 0.600 mg/mL. Add 1 mL of the above stock standard to the 1000 mL volume of sample).
 - d. Add 60 mL of Methylene Chloride.
 - e. Shake the separatory funnel for 2 minutes; venting as needed.
 - f. If an emulsion is formed, add 50 mL of saturated salt solution (NaCl) and shake again for 2 minutes, venting as needed.
 - g. Allow the organic layer to separate from the water phase for a minimum of 10 minutes.
 - h. Collect the Methylene Chloride extract into a 500 mL evaporative flask with an attached 10 mL concentrator tube - a Kuderna-Danish (K-D) concentrator (Note: The concentrator tube should already contain an ebulator).

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- i. If the emulsion interface between layers is more than one-third, the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. This may include stirring, filtration of the emulsion through a anhydrous NaSO_4 column (10 cm) or other physical methods (Note: If NaSO_4 column is used the column should be prewet with MeCl_2 and rinsed three times its volume with MeCl_2 after sample has been passed thru).
 - j. Repeat steps d, e, g and h two times more so that the sample has been extracted a total of three times, and the final volume of extract is 120 mL.
 - k. To the evaporative flask attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of Methylene Chloride to the top of the column. Place the K-D apparatus on the hot water bath set at medium 60 to 65° C. (so that the concentrator tube is partially immersed in hot water, and the entire lower rounded surface of the flask is bathed in hot vapor). At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. Complete concentration, when the volume of liquid reaches 1 mL, should require only 15-20 minutes. Once concentrated, allow the sample to cool for 10 minutes.
 - l. Rinse Snyder column with Methylene Chloride before removing, allow it to drain completely. The evaporative flask should be rinsed next and allowed to drain into the concentration tube before removing.
 - m. Add a boiling chip to the concentrator tube and attach a micro Snyder column. Place the K-D apparatus on a tube concentrator and take down to a volume of 1 mL, after rinsing down the micro Snyder column with MeCl_2 .
 - n. Transfer to a 20 mL vial with a teflon cap, properly labeled (Sample # ; B/N) and store in freezer.
2. Acid Extractions:
- a. Using 1000 mL sample, previously extracted for Base/Neutrals, adjust the pH to less than 2, using 20 mL of 1:1 Sulfuric Acid.

- Repeat steps d through m -
 - b. Transfer to a 20 mL vial with a teflon screw cap, properly labeled (Sample # ; Acid) and store in freezer.

D. Instrument Set-Up and Run:

1. Gas Chromatographic Screen for Acid Extractables. (Screen used to obtain proper dilution for sample, so it may be run on the GC/MS).

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a. Gas Chromatograph Conditions for Base/Neutrals

Initial Temp	50° C
Hold Time	2 minutes
Final Temp	300° C
Ramp Rate	8
Inject. Temp	250
Detector Temp	300 C
Chart Speed	0.5
Split Time	0.75
Split Ratio	80:1

b. Gas Chromatograph Conditions for Acid Extractions

Initial Temp	40° C
Hold Time	3.5
Final Temp	200 C
Ramp Rate	6
Inject. Temp	200° C
Detector Temp	225° C
Chart Speed	0.5
Split Time	0.50
Split Ratio	80:1

c. Instrument used for Base/Neutral and Acid Extraction Screen
Hewlett Packard 5880

d. Column Type: Capillary Column - SPB-5
CFS-4103B 30M
32-ID .25

2. Gas Chromatography/Mass Spectrometer for Base/Neutrals and Acid Extractions - Internal Standard Technique

a. Gas Chromatograph Conditions for Base and Neutrals:

Initial Temp	50
Hold Time	4
Final Temp	290
Final Time	--
Ramp	8
Inj. Temp	250
TCO	280
Aux. Temp	280
Chart Speed	0.01
Zero	10.0
FID Signal	TB
Splitless Time	0.5 min
Split Ratio	80:1

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b. Gas Chromatograph Conditions for Acid Extractions:

Initial Temp	500 C
Hold Time	4.0
Ramp	8
Final Temp	220
Inj.	200
TCD	280
AUX	280
Split Time	0.5
Split Ratio	80:1

c. Column Type: Capillary Column - SPB-5
CFS-41033 30 M
32-ID .25

d. Mass Spectrometer Conditions for Base/Neutrals:

Ion Source Temp	280
Low Mass	45
High Mass	450

e. Mass Spectrometer Conditions for Acid Extractions

Ion Source	280
Low Mass	45
High Mass	350

E. Data Handling Procedures:

1. Accuracy:

- a. Recovery of the Internal Standard
- b. % Recovery of the Q.C. Spikes

2. Precision:

- a. Duplicates
- b. Standard Curve Linearity

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3. Data Recording Procedures:

- a. The integration program (m) is used to integrate the data.
(Hewlett Packard 1000, E series, attached to the GC/MS)
- b. Hard copies of the integration are printed by the Hewlett Packard printer 9876A.
- c. The data is then reviewed by the supervisor.
- d. The data is then entered into the general laboratory computer for dissemination.

F. Reagents:

1. Refer to Federal Register, July 1, 1982, Method 625, (625-3) - Reagents.
2. Blank Water: water from a Sybron/Barnstead megohm - cm #82770 water purifying system is used.

G. Quality Control:

1. Duplicates
 - a. One duplicate analyzed for each 5 samples.
2. Blanks
 - a. One blank analyzed for each group of samples from the same site or source.
3. Spike
 - a. EPA quality control sample analyzed for each group of samples (both B/N and acid extractions). Prepared according to the sheet received with the sample, in DI water.
 - b. One sample in 20 should be spiked with the standard to determine matrix interference - % recovery..
4. Data Review
 - a. The analyst should take special care to ensure the compound of interest has not exceeded the maximum peak area count allowed by a 16-bit computer (32767 counts).
 - b. If the area count has exceeded the 32767, a secondary ion, of lesser abundance, should be selected to be targeted by the integration program. If this is not possible, then the run should be repeated on dilutions, or the data report must be prefaced with a "greater than" for a reported concentration.

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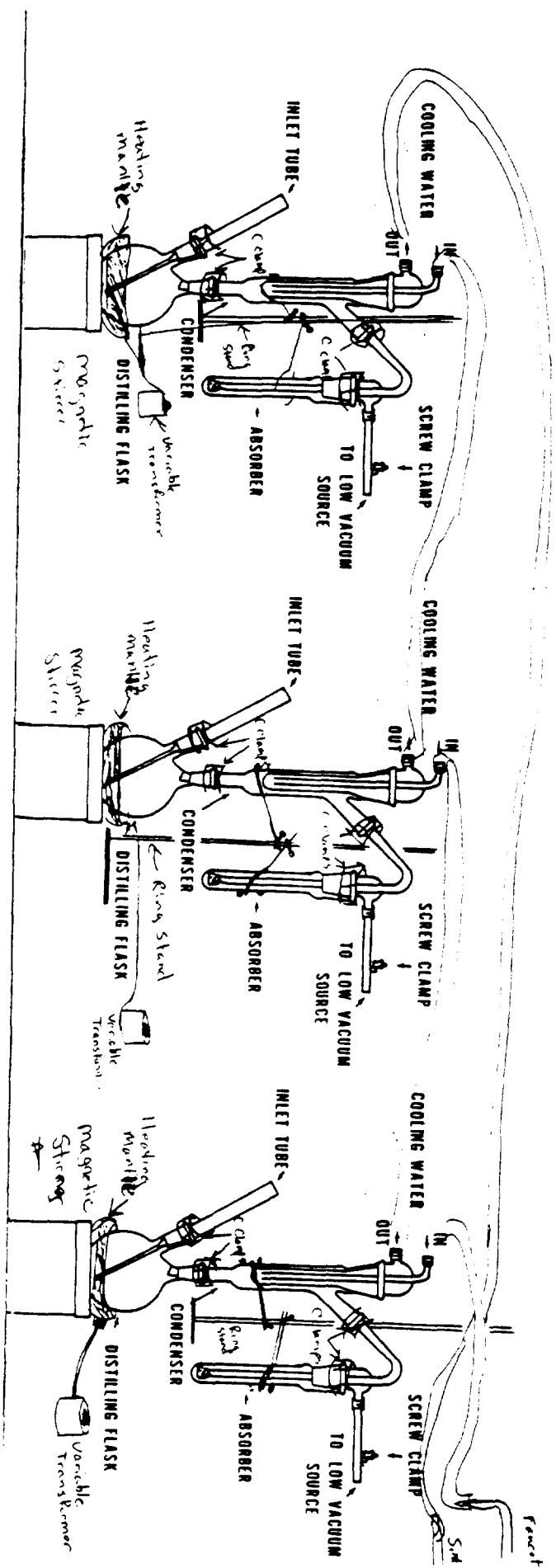
H. Washing:

All glassware used (i.e. transfer pipettes, separatory funnels, etc.) are washed with hot water and soap, rinsed well with D.I. water, and triple solvent rinsed: Acetone, Methylene Chloride and Hexane - in that order.

I. Safety:

All of Section 9.0 - Laboratory Safety - should be read before preceeding.

Diagram A



Method 625—Base/Neutrals and Acids**1. Scope and Application**

1.1 This method covers the determination of a number of organic compounds that are partitioned into an organic solvent and are amenable to gas chromatography. The parameters listed in Tables 1 and 2 may be qualitatively and quantitatively determined using this method.

1.2 The method may be extended to include the parameters listed in Table 3. Benzidine can be subject to oxidative losses during solvent concentration. Under the alkaline conditions of the extraction step, α -BHC, γ -BHC, endosulfan I and II, and endrin are subject to decomposition. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described. N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine. The preferred method for each of these parameters is listed in Table 3.

1.3 This is a gas chromatographic/mass spectrometry (GC/MS) method applicable to the determination of the compounds listed in Tables 1, 2, and 3 in municipal and industrial discharges as provided under 40 CFR 136.1.

1.4 The method detection limit (MDL) defined in Section 16.1¹ for each parameter is listed in Tables 4 and 5. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.5 Any modification to this method, beyond those expressly permitted, shall be considered as a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5. Depending upon the nature of the modification and the extent of intended use, the applicant may be required to demonstrate that the modifications will produce equivalent results when applied to relevant wastewaters.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph/mass spectrometer and in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. Summary of Method

2.1 A measured volume of sample, approximately 1-L, is serially extracted with methylene chloride at a pH greater than 11 and again at a pH less than 2 using a separatory funnel or a continuous extractor. The methylene chloride extract is dried, concentrated to a volume of 1 mL and analyzed by GC/MS. Qualitative identification of the parameters in the extract is performed using the retention time and the relative abundance of three characteristic masses (m/z). Quantitative analysis is performed using either external or internal standard techniques with a single characteristic m/z .

3. Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the total ion current profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.1.3.

3.1.1 Glassware must be scrupulously cleaned.² Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by detergent washing with hot water, and rinses with tap water and distilled water. The glassware should then be drained dry, and heated in a muffle furnace at 400 °C for 15 to 30 min. Some thermally stable materials, such as PCBs, may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Thorough rinsing with such solvents usually eliminates PCB interference. Volumetric ware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled.

3.3 The base-neutral extraction may cause significantly reduced recovery of phenol, 2-methylphenol, and 2,4-dimethylphenol. The analyst must recognize that results obtained under these conditions are minimum concentrations.

3.4 The packed gas chromatographic columns recommended for the basic fraction may not exhibit sufficient resolution for certain isomeric pairs including the following: anthracene and phenanthrene; chrysene and benzo(a)anthracene; and benzo(b)fluoranthene and benzo(k)fluoranthene. The gas chromatographic retention time and mass spectra for these pairs of compounds are not sufficiently different to make an unambiguous identification. Alternative techniques should be used to identify and quantify these specific compounds, such as Method 810.

3.5 In samples that contain an inordinate number of interferences, the use of chemical ionization (CI) mass spectrometry may make identification easier. Tables 6 and 7 give characteristic CI ions for most of the compounds covered by this method. The use of CI mass spectrometry to support electron ionization (EI) mass spectrometry is encouraged but not required.

4. Safety.

4.1 The toxicity or carcinogenicity of each reagent used in this method have not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified ** for the information of the analyst.

4.2 The following parameters covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens: benzo(a)anthracene, benzidine, 3,3'-dichlorobenzidine, benzo(a)pyrene, α -BHC, β -BHC, δ -BHC, γ -BHC, dibenzo(a,h)anthracene, N-nitrosodimethylamine, 4,4'-DDT, and polychlorinated biphenyls (PCBs). Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete or composited sampling.

5.1.1 Grab sample bottle—1-L or 1-gal. amber glass, fitted with a screw cap lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The bottle and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.1.2 Automatic sampler (optional)—The sampler must incorporate glass sample containers for the collection of a minimum of 250 mL of sample. Sample containers must be kept refrigerated at 4 °C and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used, before use, however, the compressible tubing should be thoroughly rinsed with methanol, followed by repeated rinsings with distilled water to minimize the potential for contamination of the sample. An integrating flow meter is required to collect flow proportional composites.

5.2 Glassware (All specifications are suggested. Catalog numbers are included for illustration only.):

5.2.1 Separatory funnel—2-L with Teflon stopcock.

5.2.2 Drying column—Chromatographic column, 19 mm ID, with coarse frit filter disc.

5.2.3 Concentrator tube, Kuderna-Danish—10-mL graduated (Kontes K-370050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

5.2.4 Evaporative flask, Kuderna-Danish—500-mL (Kontes K-57001-0500 or equivalent). Attach to concentrator tube with springs.

5.2.5 Snyder column, Kuderna-Danish—Three all macro (Kontes K-503000-0121 or equivalent).

5.2.6 Snyder column, Kuderna-Danish—Two-ball macro (Kontes K-569001-0219 or equivalent).

5.2.7 Vials—10 to 15-mL, amber glass, with Teflon-lined screw cap.

5.2.8 Continuous liquid—liquid extractor—Equipped with Teflon or glass connecting joints and stopcocks requiring no lubrication. (Hershberg-Wolf Extractor, Ace Glass Company, Vineland, N.J., P/N 6841-10 or equivalent.)

5.3 Boiling chips—Approximately 10/40 mesh. Heat to 400 °C for 30 min of Soxhlet extract with methylene chloride.

5.4 Water bath—Heated, with concentric ring cover, capable of temperature control ($\pm 2^\circ\text{C}$). The bath should be used in a hood.

5.5 Balance—Analytical, capable of accurately weighing 0.0001 g.

5.6 GC/MS system:

5.6.1 Gas Chromatograph—An analytical system complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases. The injection port must be designed for on-column injection when using packed columns and for splitless injection when using capillary columns.

5.6.2 Column for base/neutral—1.8 m long x 2 mm ID glass, packed with 3% SP-2250 on Supelcoport (100/120 mesh) or equivalent. This column was used to develop the method performance statements in Section 16. Guidelines for the use of alternate column packings are provided in Section 13.1.

5.6.3 Column for acids—1.8 m long x 2 mm ID glass, packed with 1% SP-1240DA on Supelcoport (100/120 mesh) or equivalent. This column was used to develop the method performance statements in Section 16. Guidelines for the use of alternate column packings are given in Section 13.1.

5.6.4 Mass spectrometer—Capable of scanning from 35 to 450 amu every 7 s or less, utilizing a 70 V (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the criteria in Table 9 when 50 ng of decafluorotriphenyl phosphine (DFTPP; bis(perfluorophenyl) phenyl phosphine) is injected through the GC inlet.

5.6.5 GC/MS interface—Any GC to MS interface that gives acceptable calibration points at 50 ng per injection for each of the parameters of interest and achieves all acceptable performance criteria (Section 12) may be used. GC to MS interfaces constructed of all glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

5.6.6 Data system—A computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for specific

m/z and plotting such m/z abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

6. Reagents

6.1 Reagent water—Reagent water is defined as a water in which an interferent is not observed at the MDL of the parameters of interest.

6.2 Sodium hydroxide solution (10 N)—Dissolve 40 g of NaOH (ACS) in reagent water and dilute to 100 mL.

6.3 Sodium thiosulfate—(ACS) Granular.

6.4 Sulfuric acid (1+1)—Slowly, add 50 mL of H₂SO₄ (ACS, sp. gr. 1.84) to 50 mL of reagent water.

6.5 Acetone, methanol, methylene chloride—Pesticide quality or equivalent.

6.6 Sodium sulfate—(ACS) Granular, anhydrous. Purify by heating at 400 °C for 4 h in a shallow tray.

6.7 Stock standard solutions (100 µg/µL)—standard solutions can be prepared from pure standard materials or purchased as certified solutions.

6.7.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in pesticide quality acetone or other suitable solvent and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

6.7.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4 °C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.7.3 Stock standard solutions must be replaced after six months, or sooner if comparison with quality control check samples indicate a problem.

6.8 Surrogate standard spiking solution—Select a minimum of three surrogate compounds from Table 8. Prepare a surrogate standard spiking solution containing each selected surrogate compound at a concentration of 100 µg/mL in acetone. Addition of 1.00 mL of this solution to 1000 mL of sample is equivalent to a concentration of 100 µg/L of each surrogate standard. Store the spiking solution at 4 °C in Teflon-sealed glass container. The solution should be checked frequently for stability. The solution must be replaced after six months, or sooner if comparison with quality control check standards indicates a problem.

6.9 DFTPP standard—Prepare a 25 µg/mL solution of DFTPP in acetone.

6.10 Quality control check sample concentrate—See Section 8.2.1.

7. Calibration

7.1 Establish gas chromatographic operating parameters equivalent to those indicated in Tables 4 or 5.

7.2 Internal standard calibration procedure—To use this approach, the analyst must select three or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standards is not affected by method or matrix interferences. Some recommended internal standards are listed in Table 8. Use the base peak m/z as the primary m/z for quantification of the standards. If interferences are noted, use one of the next two most intense masses for quantification.

7.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding appropriate volumes of one or more stock standards to a volumetric flask. To each calibration standard or standard mixture, add a known constant amount of one or more internal standards, and dilute to volume with acetone. One of the calibration standards should be at a concentration near, but above, the MDL and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC/MS system.

7.2.2 Using injections of 2 to 5 µL, analyze each calibration standard according to Section 13 and tabulate the area of the primary characteristic m/z (Tables 4 and 5) against concentration for each compound and internal standard. Calculate response factors (RF) for each compound using Equation 1.

$$RF = \frac{(A_x)(C_s)}{(A_s)(C_x)}$$

where:

A_x = Area of the characteristic m/z for the parameter to be measured.

A_s = Area of the characteristic m/z for the internal standard.

C_s = Concentration of the internal standard (µg/L).

C_x = Concentration of the parameter to be measured (µg/L).

If the RF value over the working range is a constant (<35% RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_x/A_s vs. RF.

7.3 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than $\pm 20\%$, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control

program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.1.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Sections 10.6 and 13.1) to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 Before processing any samples, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system and glassware are under control. Each time a set of samples is extracted or reagents are changed, a reagent water blank must be processed as a safeguard against laboratory contamination.

8.1.4 The laboratory must, on an ongoing basis, spike and analyze a minimum of 5% of all samples to monitor and evaluate laboratory data quality. This procedure is described in Section 8.3.

8.1.5 The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 8.4. The frequency of the check standard analyses is equivalent to 5% of all samples analyzed but may be reduced if spike recoveries from samples (Section 8.3) meet all specified quality control criteria.

8.1.6 The laboratory must maintain performance records to document the quality of data that is generated. This procedure is described in Section 8.5.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 A quality control (QC) check sample concentrate is required containing each parameter of interest at a concentration of 100 µg/mL in acetone. Multiple solutions may be required. PCBs and multicomponent pesticides may be omitted from this test. The QC check sample concentrate must be obtained from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory in Cincinnati, Ohio, if available. If not available from that source, the QC check sample concentrate must be obtained from another external source. If not available from either source above, the QC check sample concentrate must be prepared by the laboratory using stock standards

prepared independently from those used for calibration.

8.2.2 Using a pipet, prepare QC check samples at a concentration of 100 µg/L by adding 1.00 mL of QC check sample concentrate to each of four 1-L aliquots of reagent water.

8.2.3 Analyze the well-mixed QC check samples according to the method beginning in Section 10 or 11.

8.2.4 Calculate the average recovery (X) in µg/L and the standard deviation of the recovery (s) in µg/L for each parameter using the four results.

8.2.5 For each parameter compare s and X with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 6. If s and X for all parameters of interest meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual X falls outside the range for accuracy, the system performance is unacceptable for that parameter.

Note.—The large number of parameters in Table 6 present a substantial probability that one or more will fail at least one of the acceptance criteria when all parameters are analyzed.

8.2.6 When one or more of the parameters tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 8.2.6.1 or 8.2.6.2.

8.2.6.1 Locate and correct the source of the problem and repeat the test for all parameters of interest beginning with Section 8.2.2.

8.2.6.2 Beginning with Section 8.2.2, repeat the test only for those parameters that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.2.2.

8.3 The laboratory must, on an ongoing basis, spike at least 5% of the samples from each sample site being monitored to assess accuracy. For laboratories analyzing 1 to 20 samples per month, at least one spiked sample per month is required.

8.3.1 The concentration of the spike in the sample should be determined as follows:

8.3.1.1 If, as in compliance monitoring, the concentration of a specific parameter in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.2 If the concentration of a specific parameter in the sample is not being checked against a limit specific to that parameter, the spike should be at 100 µg/L or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.3 If it is impractical to determine background levels before spiking (e.g., maximum holding times will be exceeded), the spike concentration should be (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or 100 µg/L.

8.3.2 Analyze one sample aliquot to determine the background concentration (B) of each parameter. If necessary, prepare a new QC check sample concentrate (Section 8.2.1) appropriate for the background concentrations in the sample. Spike a second sample aliquot with 1.0 mL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each parameter. Calculate each percent recovery (P) as $100(A-B)/T$, where T is the known true value of the spike.

8.3.3 Compare the percent recovery (P) for each parameter with the corresponding QC acceptance criteria found in Table 6. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1. If spiking was performed at a concentration lower than 100 µg/L, the analyst must use either the QC acceptance criteria in Table 6, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of a parameter: (1) calculate accuracy (X') using the equation in Table 7, substituting the spike concentration (T) for C; (2) calculate overall precision (S') using the equation in Table 7, substituting X' for X; (3) calculate the range for recovery at the spike concentration as $(100 X' / T) \pm 2.44(100 S' / T)\%$.

8.3.4 If any individual P falls outside the designated range for recovery, that parameter has failed the acceptance criteria. A check standard containing each parameter that failed the criteria must be analyzed as described in Section 8.4.

8.4 If any parameter fails the acceptance criteria for recovery in Section 8.3, a QC check standard containing each parameter that failed must be prepared and analyzed.

Note.—The frequency for the required analysis of a QC check standard will depend upon the number of parameters being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of single-component parameters in Table 6 must be measured in the sample in Section 8.3, the probability that the analysis of a QC check standard will be required is high. In this case the QC check standard should be routinely analyzed with the spike sample.

8.4.1 Prepare the QC check standard by adding 1.0 mL of QC check sample concentrate (Sections 8.2.1 or 8.3.2) to 1 L of reagent water. The QC check standard needs only to contain the parameters that failed criteria in the test in Section 8.3.

8.4.2 Analyze the QC check standard to determine the concentration measured (A) of each parameter. Calculate each percent recovery (P₁) as $100(A/T)\%$, where T is the true value of the standard concentration.

8.4.3 Compare the percent recovery (P₁) for each parameter with the corresponding QC acceptance criteria found in Table 6. Only parameters that failed the test in Section 8.3 need to be compared with these criteria. If the recovery of any such parameter fails outside the designated range, the

laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.5 As part of the QC program for the laboratory, method accuracy for wastewater samples must be assessed and records must be maintained. After the analysis of five spiked wastewater samples as in Section 8.3, calculate the average percent recovery (\bar{P}) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent interval from $\bar{P} - 2s_p$ to $\bar{P} + 2s_p$. If $\bar{P} = 90\%$ and $s_p = 10\%$, for example, the accuracy interval is expressed as 70–110%. Update the accuracy assessment for each parameter on a regular basis (e.g. after each five to ten new accuracy measurements).

8.6 As a quality control check, the laboratory must spike all samples with the surrogate standard spiking solution as described in Section 10.2, and calculate the percent recovery of each surrogate compound.

8.7 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be pre-rinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of Tygon tubing and other potential sources of contamination.

9.2 All sampling must be iced or refrigerated at 4 °C from the time of collection until extraction. Fill the sample bottles and, if residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample and mix well. EPA Methods 330.4 and 330.5 may be used for measurement of residual chlorine. Field test kits are available for this purpose.

9.3 All samples must be extracted within 7 days of collection and completely analyzed within 40 days of extraction.

10. Separatory Funnel Extraction

10.1 Samples are usually extracted using separatory funnel techniques. If emulsions will prevent achieving acceptable solvent recovery with separatory funnel extractions, continuous extraction (Section 11) may be used. The separatory funnel extraction scheme described below assumes a sample volume of 1 L. When sample volumes of 2 L are to be extracted, use 250, 100, and 100-mL volumes of methylene chloride for the serial

extraction of the base/neutrals and 200, 100, and 100-mL volumes of methylene chloride for the acids.

10.2 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2-L separatory funnel. Pipet 1.00 mL of the surrogate standard spiking solution into the separatory funnel and mix well. Check the pH of the sample with wide-range pH paper and adjust to pH > 11 with sodium hydroxide solution.

10.3 Add 60 mL of methylene chloride to the sample bottle, seal, and shake for 30 s to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 250-mL Erlenmeyer flask. If the emulsion cannot be broken (recovery of less than 80% of the methylene chloride, corrected for the water solubility of methylene chloride), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as described in Section 11.3.

10.4 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner. Label the combined extract as the base/neutral fraction.

10.5 Adjust the pH of the aqueous phase to less than 2 using sulfuric acid. Serially extract the acidified aqueous phase three times with 60-mL aliquots of methylene chloride. Collect and combine the extracts in a 250-mL Erlenmeyer flask and label the combined extracts as the acid fraction.

10.6 For each fraction, assemble a Kuderna-Danush (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D concentrator if the requirements of Section 8.2 are met.

10.7 For each fraction, pour the combined extract through a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

10.8 Add one or two clean boiling chips and attach a three-ball Snyder column to the evaporative flask for each fraction. Prewet each Snyder column by adding about 1 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (60 to 65 °C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as

required to complete the concentration in 15 to 20 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of methylene chloride. A 5-mL syringe is recommended for this operation.

10.9 Add another one or two clean boiling chips to the concentrator tube for each fraction and attach a two-ball micro-Snyder column. Prewet the Snyder column by adding about 0.5 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (60 to 65 °C) so that the concentrator tube is partially immersed in hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches about 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with approximately 0.2 mL of acetone or methylene chloride. Adjust the final volume to 1.0 mL with the solvent. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. If the extracts will be stored longer than two days, they should be transferred to Teflon-sealed screw-cap vials and labeled base/neutral or acid fraction as appropriate.

10.10 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11. Continuous Extraction

11.1 When experience with a sample from a given source indicates that a serious emulsion problem will result or an emulsion is encountered using a separatory funnel in Section 10.3, a continuous extractor should be used.

11.2 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Check the pH of the sample with wide-range pH paper and adjust to pH > 11 with sodium hydroxide solution. Transfer the sample to the continuous extractor and using a pipet, add 1.00 mL of surrogate standard spiking solution and mix well. Add 50 mL of methylene chloride to the sample bottle, seal, and shake for 30 s to rinse the inner surface. Transfer the solvent to the extractor.

11.3 Repeat the sample bottle rinse with an additional 50 to 100-mL portion of methylene chloride and add the rinse to the extractor.

11.4 Add 200 to 500 mL of methylene chloride to the distilling flask, add sufficient reagent water to ensure proper operation, and extract for 24 h. Allow to cool, then detach the distilling flask. Dry, concentrate,

and seal the extract as in Sections 10.6 through 10.9.

11.5 Charge a clean distilling flask with 500 mL of methylene chloride and attach it to the continuous extractor. Carefully, while stirring, adjust the pH of the aqueous phase to less than 2 using sulfuric acid. Extract for 24 h. Dry, concentrate, and seal the extract as in Sections 10.6 through 10.9.

12. Daily GC/MS Performance Tests

12.1 At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see if acceptable performance criteria are achieved for DFTPP.¹⁰ Each day that benzidine is to be determined, the tailing factor criterion described in Section 12.4 must be achieved. Each day that the acids are to be determined, the tailing factor criterion in Section 12.5 must be achieved.

12.2 These performance tests require the following instrumental parameters:

Electron Energy: 70 V (nominal)
Mass Range: 35 to 450 amu
Scan Time: To give at least 5 scans per peak but not to exceed 7 s per scan.

12.3 DFTPP performance test—At the beginning of each day, inject 2 µL (50 ng) of DFTPP standard solution. Obtain a background-corrected mass spectra of DFTPP and confirm that all the key *m/z* criteria in Table 9 are achieved. If all the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved. The performance criteria must be achieved before any samples, blanks, or standards are analyzed. The tailing factor tests in Sections 12.4 and 12.5 may be performed simultaneously with the DFTPP test.

12.4 Column performance test for base/ neutrals—At the beginning of each day that the base/neutral fraction is to be analyzed for benzidine, the benzidine tailing factor must be calculated. Inject 100 ng of benzidine either separately or as a part of a standard mixture that may contain DFTPP and calculate the tailing factor. The benzidine tailing factor must be less than 3.0. Calculation of the tailing factor is illustrated in Figure 13.¹¹ Replace the column packing if the tailing factor criterion cannot be achieved.

12.5 Column performance test for acids—At the beginning of each day that the acids are to be determined, inject 50 ng of pentachlorophenol either separately or as a part of a standard mix that may contain DFTPP. The tailing factor for pentachlorophenol must be less than 5. Calculation of the tailing factor is illustrated in Figure 13.¹¹ Replace the column packing if the tailing factor criterion cannot be achieved.

13. Gas Chromatography/Mass Spectrometry

13.1 Table 4 summarizes the recommended gas chromatographic operating conditions for the base/neutral fraction. Table 5 summarizes the recommended gas chromatographic operating conditions for the acid fraction. Included in these tables are retention times and MDL that can be achieved under these conditions. Examples of separations achieved by these columns

are shown in Figures 1 through 12. Other packed or capillary (open-tubular) columns or chromatographic conditions may be used if the requirements of Section 8.2 are met.

13.2 After conducting the GC/MS performance tests in Section 12, calibrate the system daily as described in Section 7.

13.3 If the internal standard calibration procedure is being used, the internal standard must be added to sample extract and mixed thoroughly immediately before injection into the instrument. This procedure minimizes losses due to adsorption, chemical reaction or evaporation.

13.4 Inject 2 to 5 µL of the sample extract or standard into the GC/MS system using the solvent-flush technique.¹² Smaller (1.0 µL) volumes may be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 µL.

13.5 If the response for any *m/z* exceeds the working range of the GC/MS system, dilute the extract and reanalyze.

13.6 Perform all qualitative and quantitative measurements as described in Sections 14 and 15. When the extracts are not being used for analyses, store them refrigerated at 4°C, protected from light in screw-cap vials equipped with unpierced Teflon-lined septa.

14. Qualitative Identification

14.1 Obtain EICPs for the primary *m/z* and the two other masses listed in Tables 4 and 5. See Section 7.3 for masses to be used with internal and surrogate standards. The following criteria must be met to make a qualitative identification:

14.1.1 The characteristic masses of each parameter of interest must maximize in the same or within one scan of each other.

14.1.2 The retention time must fall within ±30 s of the retention time of the authentic compound.

14.1.3 The relative peak heights of the three characteristic masses in the EICPs must fall within ±20% of the relative intensities of these masses in a reference mass spectrum. The reference mass spectrum can be obtained from a standard analyzed in the GC/MS system or from a reference library.

14.2 Structural isomers that have very similar mass spectra and less than 30 s difference in retention time, can be explicitly identified only if the resolution between authentic isomers in a standard mix is acceptable. Acceptable resolution is achieved if the baseline to valley height between the isomers is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

15. Calculations

15.1 When a parameter has been identified, the quantitation of that parameter will be based on the integrated abundance from the EICP of the primary characteristic *m/z* in Tables 4 and 5. Use the base peak *m/z* for internal and surrogate standards. If the sample produces an interference for the primary *m/z*, use a secondary characteristic *m/z* to quantitate.

Calculate the concentration in the sample using the response factor (RF) determined in Section 7.2.2 and Equation 3.

Equation 3.

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A_s)(I_i)}{(A_i)(\text{RF})(V_e)}$$

where:

A_s = Area of the characteristic *m/z* for the parameter or surrogate standard to be measured.

A_i = Area of the characteristic *m/z* for the internal standard.

I_i = Amount of internal standard added to each extract (µg).

V_e = Volume of water extracted (L).

15.2 Report results in µg/L without correction for recovery data. All QC data obtained should be reported with the sample results.

16. Method Performance

16.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.¹³ The MDL concentrations listed in Tables 4 and 5 were obtained using reagent water.¹⁴ The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

16.2 This method was tested by 15 laboratories using reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5 to 1300 µg/L.¹⁴ Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 7.

17. Screening Procedure for 2,3,7,8-Tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD)

17.1 If the sample must be screened for the presence of 2,3,7,8-TCDD, it is recommended that the reference material not be handled in the laboratory unless extensive safety precautions are employed. It is sufficient to analyze the base/neutral extract by selected ion monitoring (SIM) GC/MS techniques, as follows:

17.1.1 Concentrate the base/neutral extract to a final volume of 0.2 mL.

17.1.2 Adjust the temperature of the base/neutral column (Section 5.6.2) to 220 °C.

17.1.3 Operate the mass spectrometer to acquire data in the SIM mode using the ions at *m/z* 257, 320 and 322 and a dwell time no greater than 333 milliseconds per mass.

17.1.4 Inject 5 to 7 µL of the base/neutral extract. Collect SIM data for a total of 10 min.

17.1.5 The possible presence of 2,3,7,8-TCDD is indicated if all three masses exhibit simultaneous peaks at any point in the selected ion current profiles.

17.1.6 For each occurrence where the possible presence of 2,3,7,8-TCDD is indicated, calculate and retain the relative abundances of each of the three masses.

17.2 False positives to this test may be caused by the presence of single or coeluting combinations of compounds whose mass spectra contain all of these masses.

17.3 Conclusive results of the presence and concentration level of 2,3,7,8-TCDD can

TABLE 4.—CHROMATOGRAPHIC CONDITIONS, METHOD DETECTION LIMITS, AND CHARACTERISTIC MASSES FOR BASE/NEUTRAL EXTRACTABLES—
Continued

Parameter	Reten- tion time (min)	Method detection limit (µg/L)	Characteristic masses					
			Electron impact			Chemical ionization		
			Primary	Second- ary	Second- ary	Meth- ane	Meth- ane	Meth- ane
Acenaphthene	17.8	1.8	154	153	152	154	156	183
Dimethyl phthalate	18.3	1.8	183	184	184	151	183	184
2,5-Dinitrotoluene	18.7	1.8	185	88	121	183	211	223
Fluorene	18.5	1.8	166	166	167	166	167	186
4-Chlorophenyl phenyl ether	18.5	4.2	204	208	141			
2,4-Dinitrotoluene	19.9	5.7	166	83	182	183	211	223
Dibenzophthalate	20.1	1.8	149	177	150	177	223	251
N-Nitrosodimethylamine*	20.5	1.8	189	188	187	188	170	198
Hexachlorobenzene	21.0	1.8	284	142	249	284	286	288
β-BHC*	21.1		183	181	108			
4-Bromophenyl phenyl ether	21.2	1.8	248	250	141	249	251	277
γ-BHC*	22.4		183	181	108			
Phenanthrene	22.6	5.4	178	178	176	178	178	207
Anthracene	22.8	1.8	178	178	176	178	178	207
β-BHC	23.4	4.2	181	83	108			
Heptachlor	23.4	1.8	100	272	274			
γ-BHC	23.7	3.1	183	108	181			
Aldrin	24.0	1.8	86	263	229			
Octyl phthalate	24.7	2.5	149	150	104	149	206	278
Heptachlor epoxide	25.6	2.2	353	355	351			
Endosulfan I*	26.4		237	338	341			
Fluoranthene	26.5	2.2	202	101	100	203	231	243
Declon	27.2	2.5	79	283	278			
4,4'-DDE	27.2	5.8	246	248	178			
Pyrene	27.3	1.8	202	101	100	203	231	243
Endrin*	27.9		81	263	82			
Endosulfan II*	28.6		237	338	341			
4,4'-DDD	28.6	2.8	235	237	165			
Benzene*	28.8	4.4	78	92	185	185	213	225
4,4'-DDT	29.3	4.7	235	237	165			
Endosulfan sulfate	29.6	5.6	272	387	422			
Endrin isobutylate			87	345	250			
Butyl benzyl phthalate	29.8	2.5	148	81	208	148	298	327
3,3'-Diethylbiphenyl	30.6	2.5	148	197	278	148		
Chrysene	31.5	2.5	228	228	229	228	229	257
Benzo[a]anthracene	31.5	7.8	228	229	228	228	229	257
3,3'-Dichlorobenzidine	32.2	18.5	252	254	128			
Dimethyl phthalate	32.5	2.5	149					
Benzo[b]fluoranthene	34.9	4.8	252	253	125	252	253	281
Benzo[k]fluoranthene	34.9	2.5	252	253	125	252	253	281
Benzo[a]pyrene	36.4	2.5	252	253	125	252	253	281
Indeno[1,2,3-cd]pyrene	42.7	3.7	275	138	277	276	277	306
Dibenz[a,h]anthracene	43.2	2.5	275	138	278	276	278	307
Benzo[ghi]perylene	45.1	4.1	276	138	277	276	277	306
N-Nitrosodimethylamine*			42	74	44			
Chlordane*	18-30		373	375	377			
Toxaphene*	25-34		158	231	233			
PCB 1018*	18-30		224	260	294			
PCB 1221*	18-30	30	190	224	290			
PCB 1232*	15-32		190	224	290			
PCB 1242*	15-32		224	260	294			
PCB 1248*	12-34		294	300	262			
PCB 1254*	23-34	38	294	300	262			
PCB 1260*	23-32		300	362	394			

* See Section 1.2.

* These compounds are mixtures of various isomers. (See figures 2 thru 12.)

Column conditions: Supelcoport 100/120 mesh coated with 3% SP-2250 packed in a 1.8 m long x 2mm ID glass column with helium carrier gas at 30 mL/min flow rate. Column temperature held isothermal at 50 °C for 4 min, then programmed at 8 °C/min to 270 °C and held for 30 min.

TABLE 5.—CHROMATOGRAPHIC CONDITIONS, METHOD DETECTION LIMITS, AND CHARACTERISTIC MASSES FOR ACID EXTRACTABLES

Parameter	Reten- tion time (min)	Method detection limit (µg/L)	Characteristic masses					
			Electron impact			Chemical ionization		
			Primary	Second- ary	Second- ary	Meth- ane	Meth- ane	Meth- ane
2-Chlorophenol	5.9	3.3	126	64	130	126	131	187
2-Nitrophenol	6.3	3.8	136	95	109	140	188	122
Phenol	8.0	1.5	94	95	96	96	123	135
2,4-Dimethylphenol	9.4	2.7	122	107	121	123	151	183
2,4-Dichlorophenol	9.8	2.7	182	184	98	183	186	187
2,4,6-Trichlorophenol	11.8	2.7	196	198	200	197	199	201
4-Chloro-3-methylphenol	13.2	3.0	142	107	144	143	171	183
2,6-Dinitrophenol	15.9	42	184	83	154	185	213	225
2-Methyl-4-nitrophenol	16.2	24	198	182	77	198	227	239
Pentachlorophenol	17.5	3.8	296	294	268	297	265	288
4-Nitrophenol	20.3	2.4	85	139	108	140	188	122

Column conditions: Supelcoport 100/120 mesh coated with 1% SP-1240DA packed in a 1.8 m long x 2mm ID glass column with helium carrier gas at 30 mL/min flow rate. Column temperature held isothermal at 70 °C for 2 min then programmed at 8 °C/min to 200 °C.

TABLE 6.—QC ACCEPTANCE CRITERIA—METHOD 625

Parameter	Test conclusion ($\mu\text{g/L}$)	Limits for σ ($\mu\text{g/L}$)	Range for \bar{x} ($\mu\text{g/L}$)	Range for P, Percent
Acenaphthene	100	27.6	80.1-132.3	47-145
Acenaphthylene	100	40.2	53.5-126.0	33-145
Adren	100	39.0	7.2-152.2	0-100
Anthracene	100	32.0	43.4-116.0	27-133
Benzofluoranthene	100	27.6	41.8-133.0	33-143
Benzofluoranthene	100	36.8	42.0-140.4	24-150
Benzofluoranthene	100	32.3	25.2-145.7	11-102
Benzofluoranthene	100	38.0	31.7-148.0	17-103
Benzofluoranthene	100	56.8	0-195.0	0-219
Benzofluoranthene	100	23.4	0-138.9	0-152
Benzofluoranthene	100	31.5	41.5-130.6	24-149
Benzofluoranthene	100	21.6	0-100.0	0-110
Benzofluoranthene	100	55.0	42.9-126.0	12-150
Benzofluoranthene	100	34.5	49.2-164.7	33-184
Benzofluoranthene	100	48.3	52.9-138.6	38-180
Benzofluoranthene	100	41.1	28.9-133.8	8-150
Benzofluoranthene	100	23.0	54.9-114.4	33-127
Benzofluoranthene	100	13.0	54.5-113.5	60-118
Benzofluoranthene	100	33.4	38.4-144.7	25-150
Benzofluoranthene	100	48.3	44.1-139.9	17-100
Benzofluoranthene	100	31.5	0-134.5	0-145
Benzofluoranthene	100	32.0	19.2-119.7	4-130
Benzofluoranthene	100	61.6	0-170.6	0-203
Benzofluoranthene	100	70.0	0-199.7	0-227
Benzofluoranthene	100	16.7	8.4-111.0	1-116
Benzofluoranthene	100	30.9	48.4-112.0	32-129
Benzofluoranthene	100	41.7	18.7-152.9	0-172
Benzofluoranthene	100	32.1	37.3-105.7	20-124
Benzofluoranthene	100	71.4	8.2-212.5	0-262
Benzofluoranthene	100	30.7	44.3-119.3	29-130
Benzofluoranthene	100	26.5	0-100.0	0-114
Benzofluoranthene	100	23.2	0-100.0	0-112
Benzofluoranthene	100	21.8	47.5-125.9	39-130
Benzofluoranthene	100	25.6	60.1-136.7	50-156
Benzofluoranthene	100	31.4	18.6-121.8	4-146
Benzofluoranthene	100	16.7	0-103.5	0-107
Benzofluoranthene	100	32.5	0-166.6	0-200
Benzofluoranthene	100	32.8	42.9-121.3	26-137
Benzofluoranthene	100	20.7	71.6-108.4	56-121
Benzofluoranthene	100	37.2	0-172.2	0-182
Benzofluoranthene	100	54.7	70.9-109.4	28-156
Benzofluoranthene	100	24.9	7.9-141.5	0-152
Benzofluoranthene	100	29.3	37.9-102.2	24-116
Benzofluoranthene	100	24.5	55.2-100.0	40-113
Benzofluoranthene	100	44.6	0-150.9	0-171
Benzofluoranthene	100	53.3	46.6-160.2	21-190
Benzofluoranthene	100	30.1	35.9-119.6	21-133
Benzofluoranthene	100	39.3	54.3-157.6	35-180
Benzofluoranthene	100	95.4	13.6-197.9	0-220
Benzofluoranthene	100	54.2	18.3-121.0	0-164
Benzofluoranthene	100	20.8	65.2-108.7	54-120
Benzofluoranthene	100	25.2	68.6-100.0	52-115
Benzofluoranthene	100	28.1	57.3-129.2	44-142
Benzofluoranthene	100	37.2	40.6-127.8	22-147
Benzofluoranthene	100	26.7	36.2-120.4	23-134
Benzofluoranthene	100	26.4	52.5-121.7	39-138
Benzofluoranthene	100	28.1	41.8-108.0	32-119
Benzofluoranthene	100	48.8	0-172.3	0-191
Benzofluoranthene	100	23.2	53.0-100.0	0-101
Benzofluoranthene	100	35.2	45.0-166.7	29-182
Benzofluoranthene	100	47.2	13.0-106.5	0-132
Benzofluoranthene	100	48.8	28.1-151.8	14-176
Benzofluoranthene	100	23.8	15.6-100.0	5-112
Benzofluoranthene	100	31.7	52.6-129.2	37-144

σ = Standard deviation for four recovery measurements, in $\mu\text{g/L}$, Section 8.2.4.

\bar{x} = Average recovery for four recovery measurements, in $\mu\text{g/L}$, Section 8.2.4.

P, Percent recovery measured, Section 8.3.2, Section 8.4.2.

Q = Detected, result must be greater than zero.

Note: These criteria are based directly upon the method performance data in Table 7. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 7.

TABLE 7. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION—METHOD 625

Parameter	Accuracy as recovery, \bar{x} ($\mu\text{g/L}$)	Single element precision, S ($\mu\text{g/L}$)	Overall precision, S ($\mu\text{g/L}$)
Acenaphthene	0.08C-0.19	0.15X-0.12	0.21X-0.67
Acenaphthylene	0.09C-0.74	0.24X-1.08	0.26X-0.54
Adren	0.79C-1.98	0.27X-1.29	0.43X-1.13
Anthracene	0.90C-0.88	0.21X-0.32	0.27X-0.64
Benzofluoranthene	0.88C-0.80	0.15X-0.80	0.26X-0.29
Benzofluoranthene	0.90C-1.90	0.22X-0.42	0.29X-0.98
Benzofluoranthene	0.87C-1.58	0.19X-1.00	0.35X-0.48
Benzofluoranthene	0.90C-0.13	0.22X-0.48	0.32X-1.28
Benzofluoranthene	0.98C-0.88	0.26X-2.40	0.51X-0.64
Benzofluoranthene	0.88C-1.64	0.18X-0.94	0.53X-0.98
Benzofluoranthene	0.87C-0.84	0.20X-0.58	0.30X-1.34
Benzofluoranthene	0.79C-1.06	0.34X-0.88	0.67X-0.17
Benzofluoranthene	0.88C-1.54	0.35X-0.98	0.56X-0.19

TABLE 7. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION—METHOD 625—Continued

Parameter	Accuracy as recovery, \bar{X} (μg/L)	Single analyst precision, S_x (μg/L)	Overall precision, S (μg/L)
Bis(2-chloroethoxy)methane	1.12C-5.04	0.16X-1.34	0.26X-2.01
Bis(2-chloroisopropyl)ether	1.03C-2.31	0.24X-0.28	0.25X-1.04
Bis(2-ethylhexyl)phthalate	0.84C-1.18	0.26X-0.73	0.36X-0.87
4-Bromophenyl phenyl ether	0.91C-1.34	0.13X-0.66	0.18X-0.88
2-Chloronaphthalene	0.89C-0.01	0.07X-0.52	0.13X-0.34
4-Chlorophenyl phenyl ether	0.91C-0.53	0.20X-0.84	0.30X-0.46
Chrysene	0.93C-1.00	0.25X-0.13	0.33X-0.08
4,4'-DDD	0.56C-0.40	0.25X-0.32	0.66X-0.98
4,4'-DDE	0.70C-0.54	0.25X-1.17	0.39X-0.04
4,4'-DDT	0.79C-3.28	0.42X-0.19	0.65X-0.58
Dibenz(a,h)anthracene	0.86C-4.72	0.30X-8.51	0.59X-0.25
O-n-butyl phthalate	0.59C-0.71	0.13X-1.16	0.29X-0.60
1,2-Dichlorobenzene	0.80C-0.28	0.20X-0.47	0.24X-0.38
1,3-Dichlorobenzene	0.86C-0.70	0.25X-0.68	0.41X-0.11
1,4-Dichlorobenzene	0.73C-1.47	0.24X-0.23	0.29X-0.38
3,3'-Dichlorobenzidine	1.23C-12.65	0.29X-7.30	0.47X-3.45
Dieldrin	0.82C-0.18	0.20X-0.18	0.25X-0.07
Diethyl phthalate	0.43C-1.00	0.25X-1.44	0.52X-0.22
Dimethyl phthalate	0.29C-1.00	0.54X-0.19	1.05X-0.92
2,4-Dinitrophenol	0.92C-4.81	0.12X-1.36	0.21X-1.50
2,5-Dinitrophenol	1.06C-3.80	0.14X-1.26	0.19X-0.35
O-n-octylphthalate	0.75C-0.79	0.21X-1.18	0.37X-1.19
Endosulfan sulfate	0.39C-0.41	0.12X-2.47	0.62X-1.03
Endrin aldehyde	0.76C-3.86	0.18X-3.81	0.73X-0.62
Fluoranthene	0.81C-1.10	0.22X-0.73	0.28X-0.60
Fluorene	0.90C-0.00	0.12X-0.28	0.13X-0.81
Heptachlor	0.87C-2.37	0.24X-0.56	0.50X-0.23
Heptachlor epoxide	0.92C-1.87	0.30X-0.46	0.28X-0.64
Heptachlorobenzene	0.74C-0.66	0.18X-0.10	0.43X-0.52
Heptachlorobutadiene	0.71C-1.01	0.19X-0.92	0.26X-0.48
Heptachlorothene	0.72C-0.83	0.17X-0.67	0.17X-0.80
Indenyl 2,3-dichlorine	0.78C-3.10	0.29X-1.48	0.50X-0.44
Isomazone	1.12C-1.41	0.27X-0.77	0.33X-0.26
Naphthalene	0.76C-1.58	0.21X-0.41	0.30X-0.68
Nitrobenzene	1.09C-3.35	0.15X-0.92	0.27X-0.21
N-nitrosodimethylamine	1.12C-6.22	0.27X-0.58	0.44X-0.47
PCB-1250	0.91C-10.96	0.35X-3.61	0.43X-1.82
Phenanthrene	0.87C-0.08	0.12X-0.57	0.15X-0.25
Pyrene	0.84C-0.16	0.16X-0.06	0.15X-0.31
1,2,4-Trichlorobenzene	0.94C-0.79	0.15X-0.85	0.21X-0.39
4-Chloro-3-methylphenol	0.54C-0.35	0.23X-0.75	0.29X-1.31
2-Chlorophenol	0.79C-0.29	0.19X-1.48	0.29X-0.97
2,4-Dichlorophenol	0.87C-0.13	0.15X-1.25	0.21X-1.28
2,4-Dimethoxyphenol	0.71C-4.41	0.16X-1.21	0.22X-1.31
2,4-Dinitrophenol	0.81C-16.04	0.38X-2.36	0.42X-26.29
2-Methyl-4,6-dinitrophenol	1.34C-28.04	0.10X-42.29	0.26X-23.10
2-Nitrophenol	1.07C-1.15	0.16X-1.94	0.27X-2.60
4-Nitrophenol	0.61C-1.22	0.38X-2.57	0.44X-3.24
Pentachlorophenol	0.93C-1.99	0.24X-3.03	0.30X-4.33
Phenol	0.43C-1.26	0.25X-0.73	0.35X-0.58
2,4,6-Trichlorophenol	0.91C-0.18	0.16X-2.22	0.22X-1.81

\bar{X} = Expected recovery for one or more measurements of a sample containing a concentration of C in μg/L.
 S_x = Expected single analyst standard deviation of measurements at an average concentration found of \bar{X} in μg/L.
 S = Expected interlaboratory standard deviation of measurements at an average concentration found of \bar{X} in μg/L.
 C = True value for the concentration in μg/L.
 X = Average recovery found for measurements of samples containing a concentration of C in μg/L.

TABLE 8.—SUGGESTED INTERNAL AND SURROGATE STANDARDS

Base/neutral fraction	Acid fraction
Anthracene	2-Fluorophenol
Anthracene-d ₈	Pentafluorophenol
Benz(a)anthracene	Phenol
4-(6-Bromodiphenyl)-4,4'	2-Pentafluoromethyl phenol
4,4'	
Chlorodibenzofluoranthene	
Decafluorobiphenyl	
2,2'-Difluorobiphenyl	
4-Fluorobiphenyl	
1-Fluorobiphenyl	
2-Fluorobiphenyl	
Naphthalene	
Naphthalene-d ₈	
2,3,4,5,6-Pentafluorobiphenyl	
Phenanthrene	
Pyrene	

TABLE 9.—OTHER KEY MASSES AND ABUNDANCE CRITERIA

Mass	m/z abundance criteria
51	30-60 percent of mass 198
59	Less than 2 percent of mass 69
77	Less than 2 percent of mass 69
127	40-60 percent of mass 198
197	Less than 1 percent of mass 198
198	Base peak, 100 percent relative abundance
199	5-8 percent of mass 198
275	10-30 percent of mass 198
365	Greater than 1 percent of mass 198
441	Present but less than mass 443
442	Greater than 40 percent of mass 198
443	17-23 percent of mass 442

BILLING CODE 1560-50-01

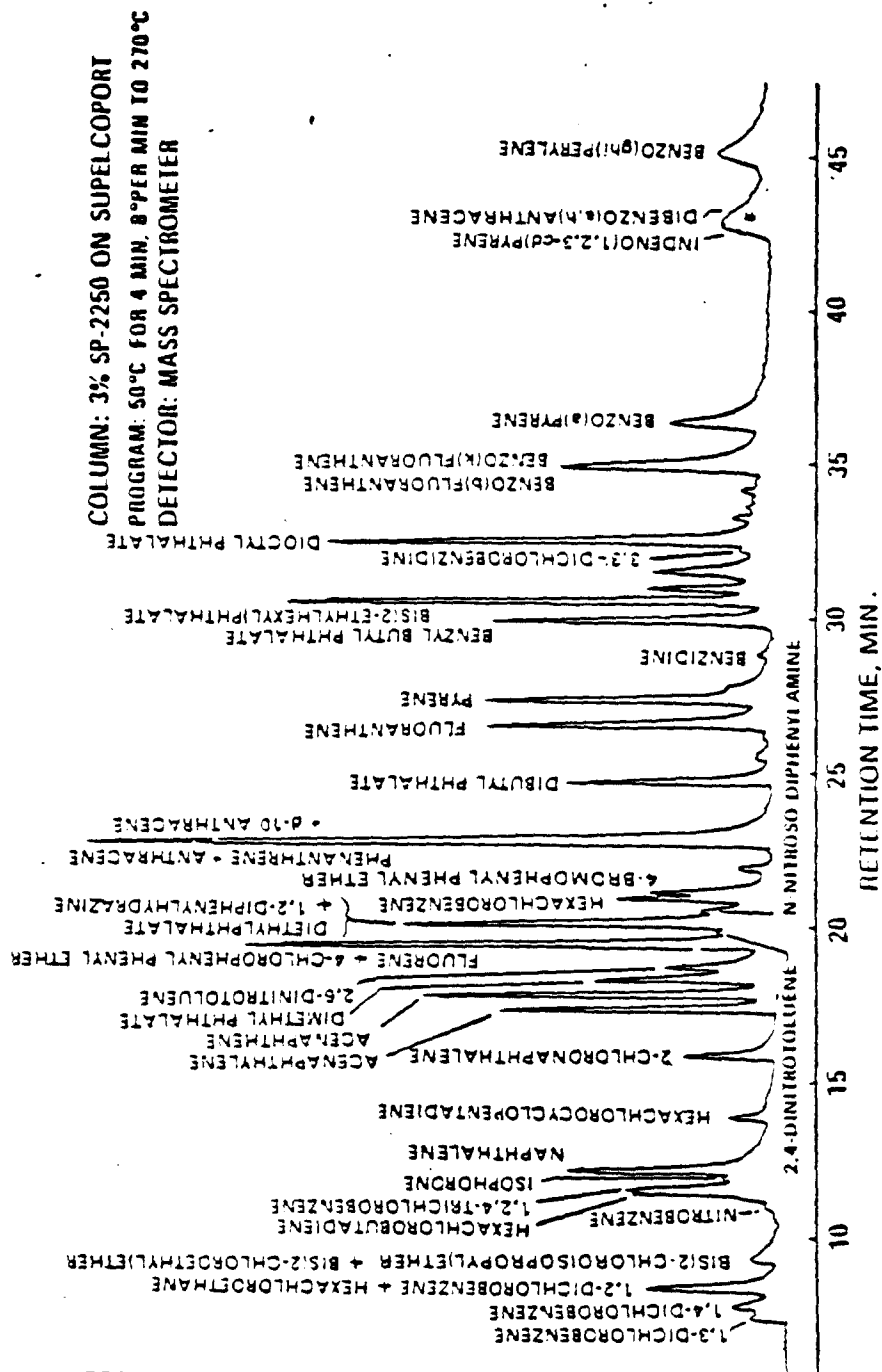


Figure 1. Gas chromatogram of base/neutral fraction.

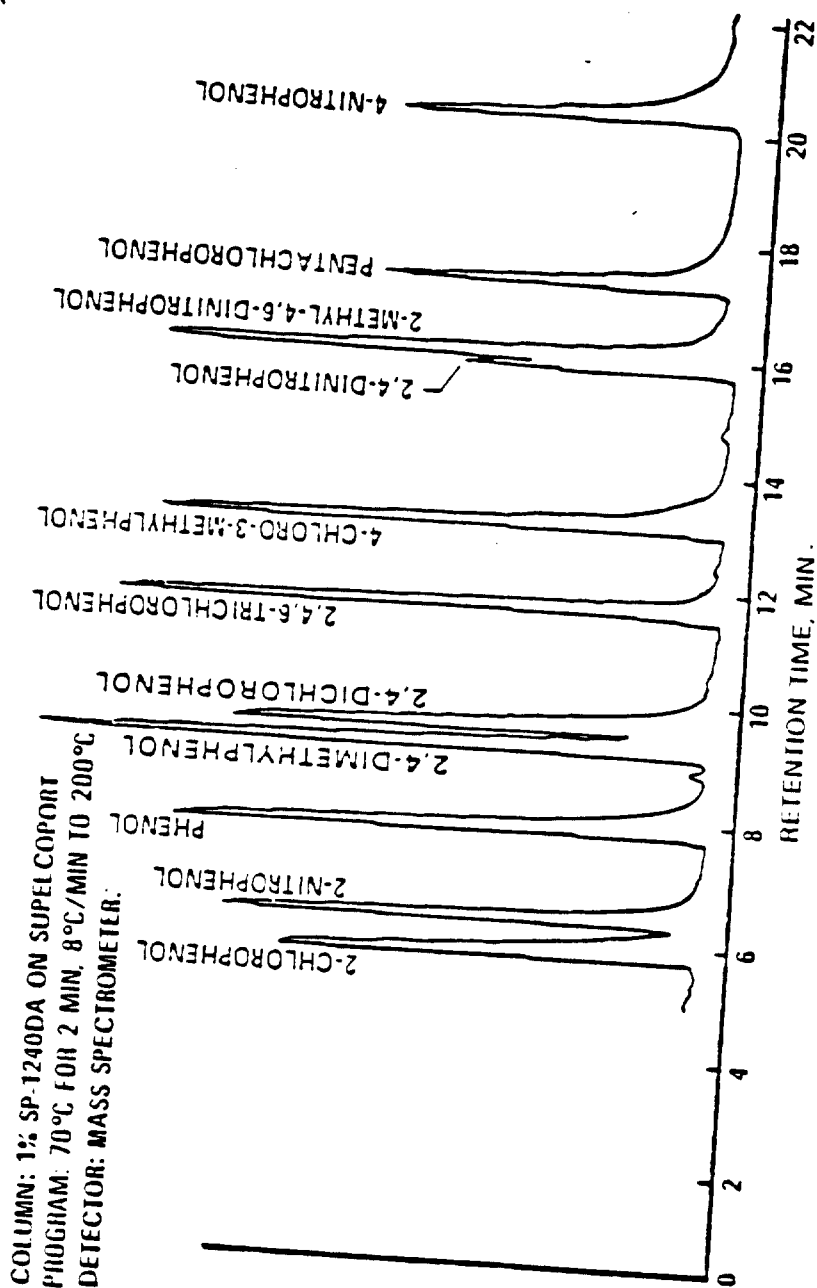


Figure 2. Gas chromatogram of acid fraction.

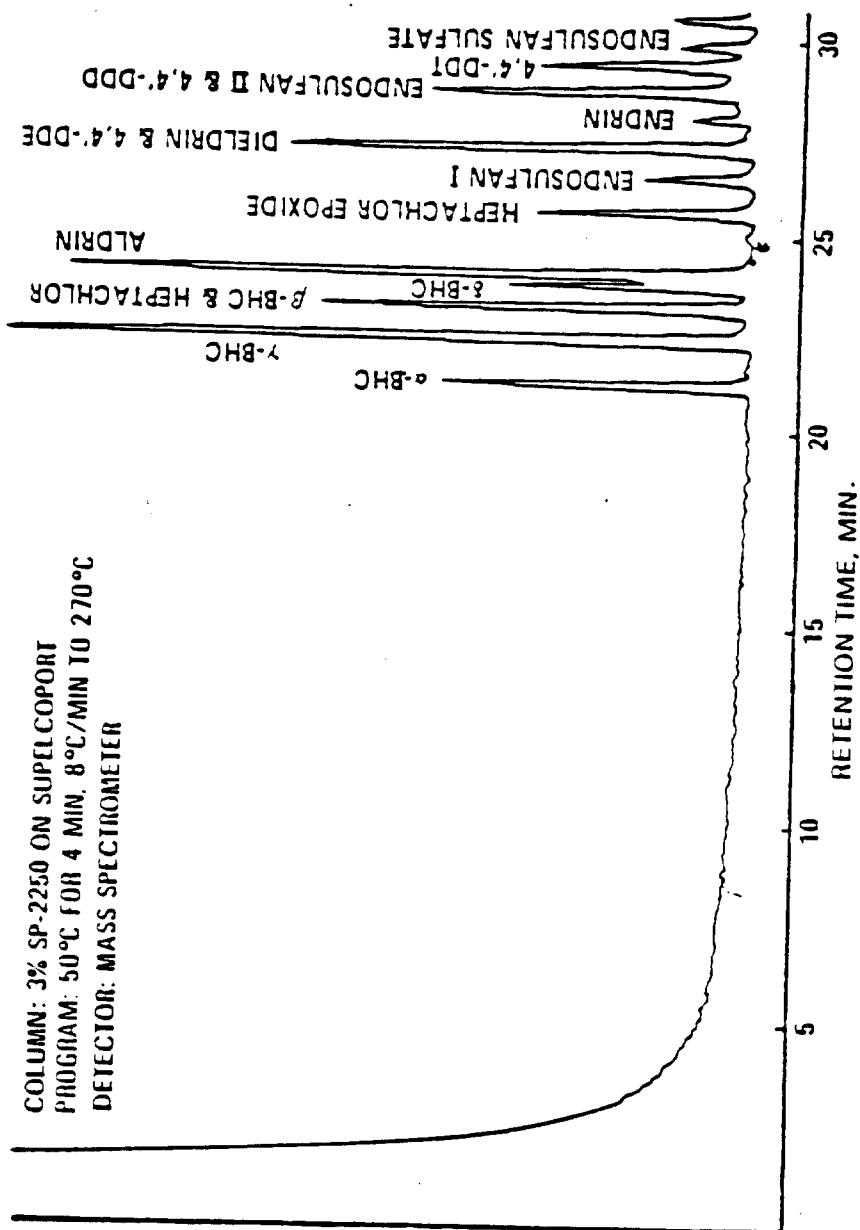


Figure 3. Gas chromatogram of pesticide fraction.

COLUMN: 3% SP-2250 ON SUPELCOPORT
PROGRAM: 50°C FOR 4 MIN, 8°C/MIN TO 270°C
DETECTOR: MASS SPECTROMETER

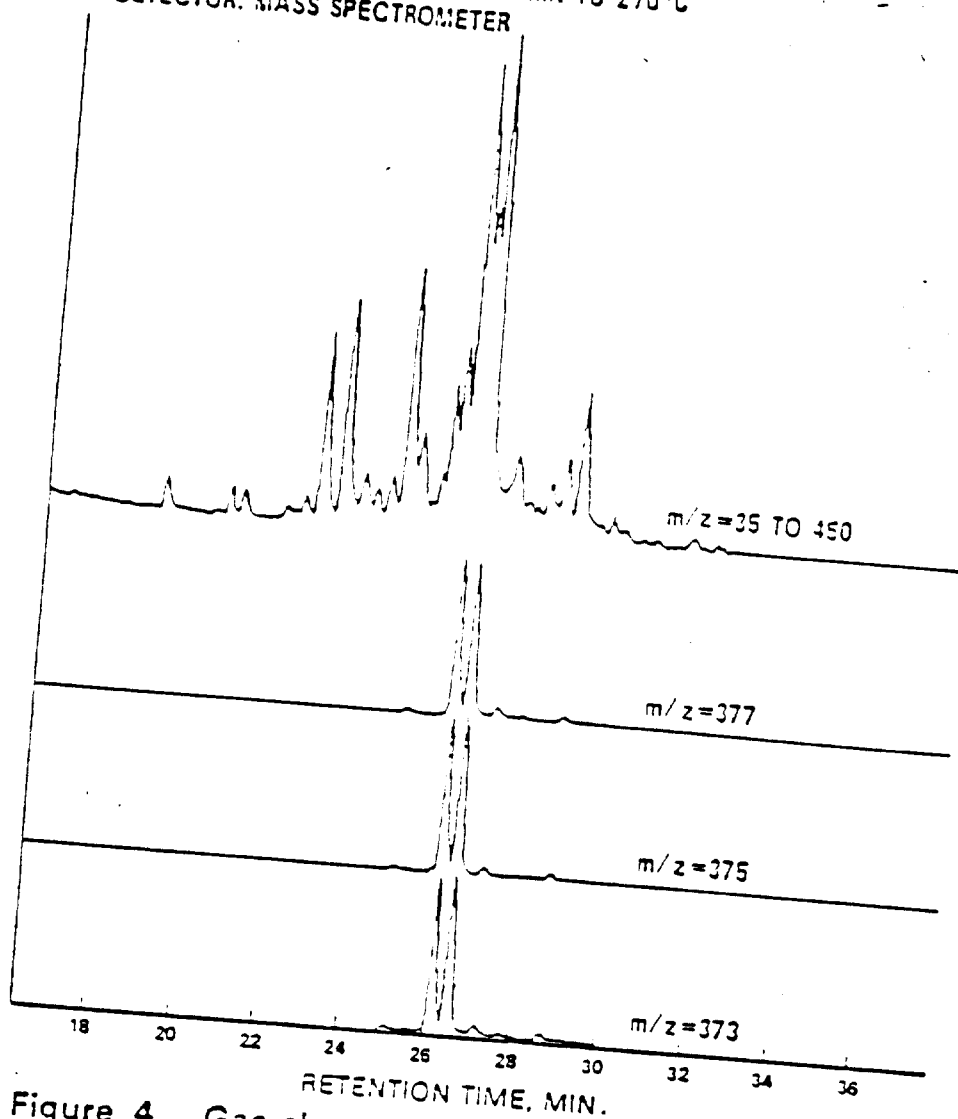


Figure 4. Gas chromatogram of chlordane.

COLUMN: 3% SP-2250 ON SUPELCOPORT
PROGRAM: 50°C FOR 4 MIN, 8°C/MIN TO 270°C
DETECTOR: MASS SPECTROMETER

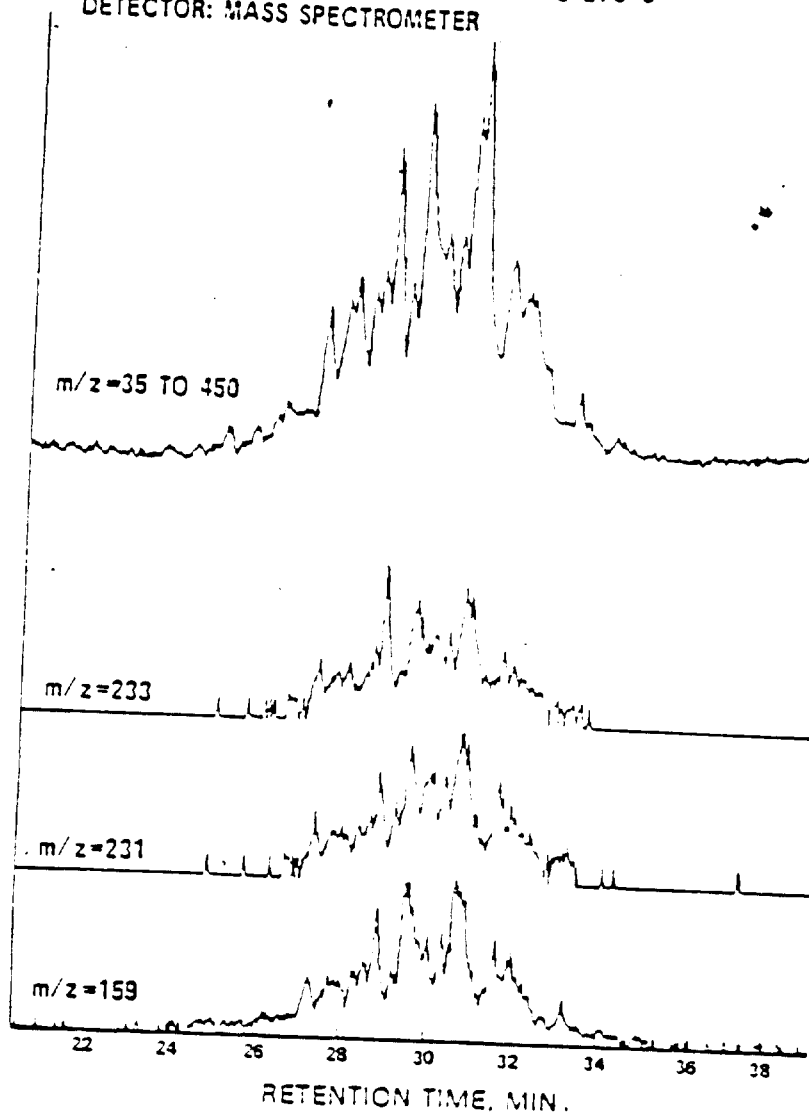


Figure 5. Gas chromatogram of toxaphene.

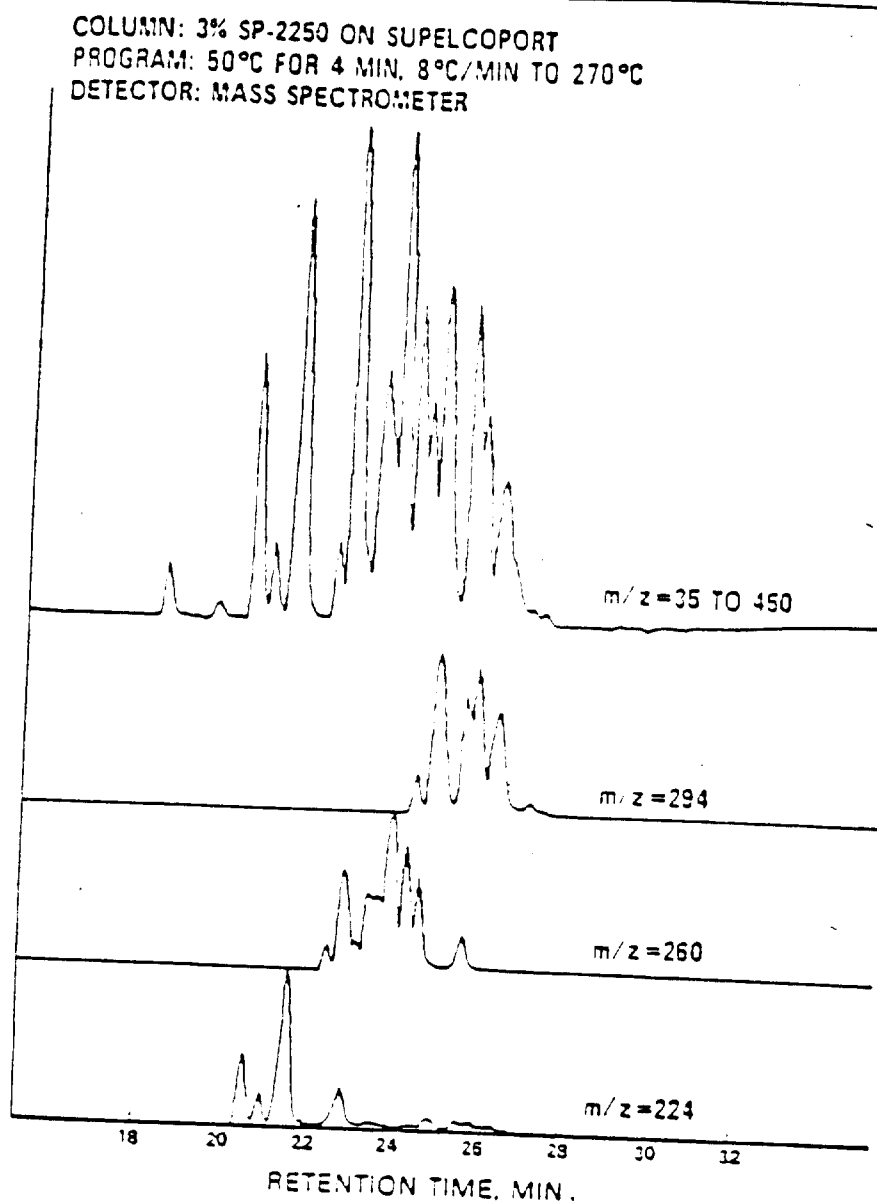


Figure 6. Gas chromatogram of PCB-1016.

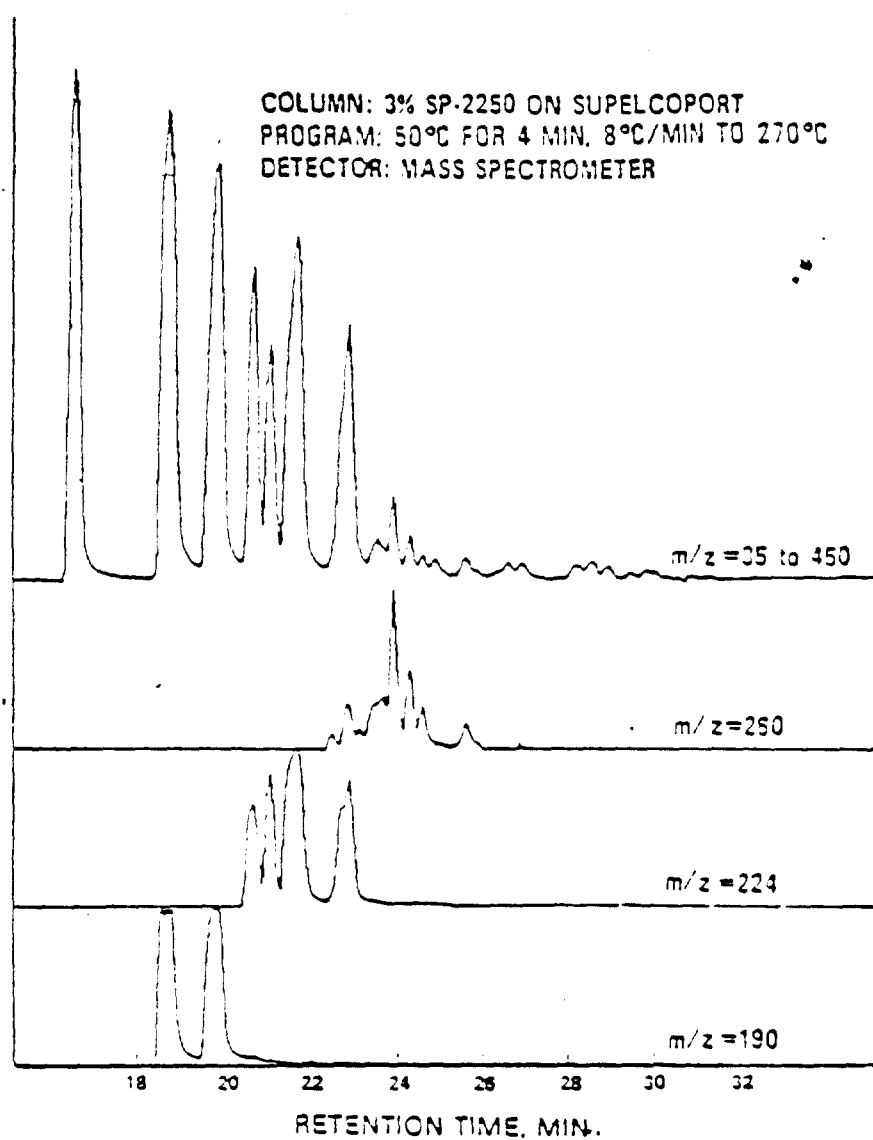


Figure 7. Gas chromatogram of PCB-1221.

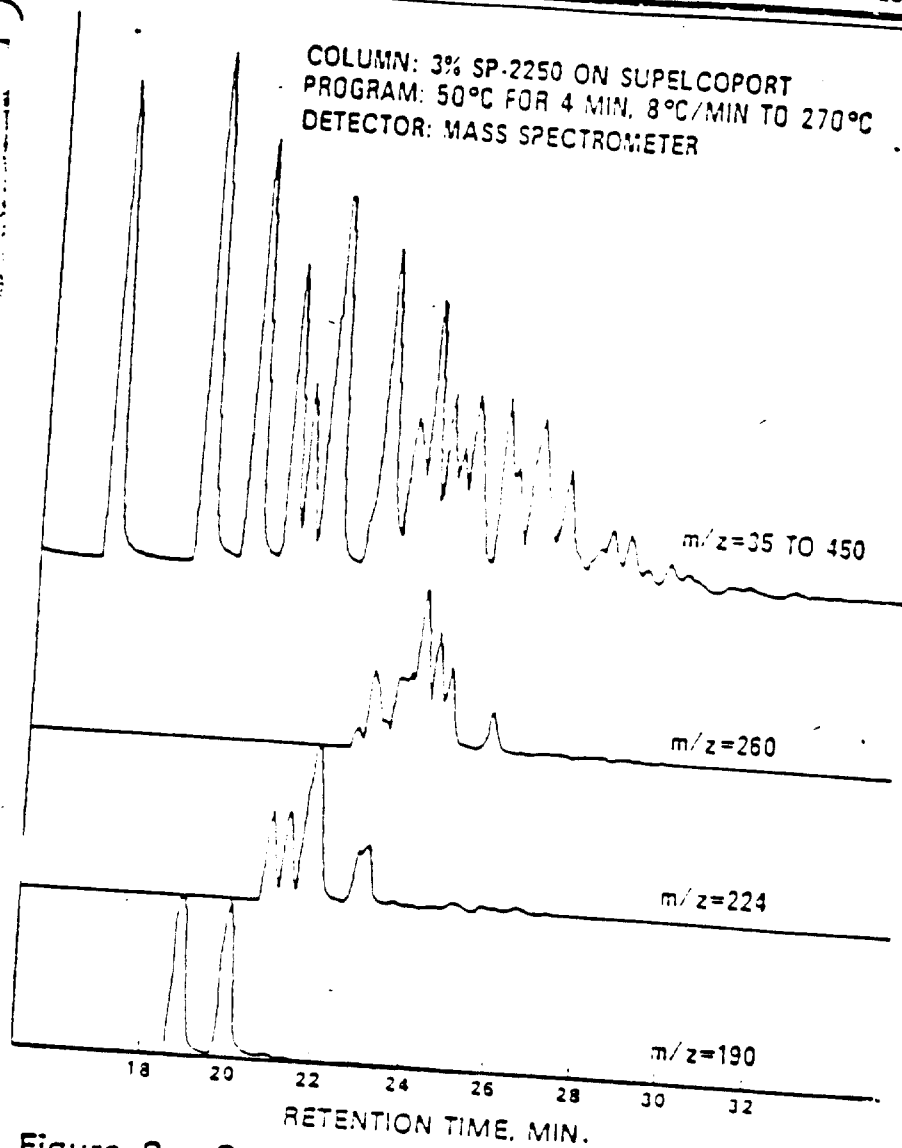


Figure 8. Gas chromatogram of PCB-1232.

COLUMN: 3% SP-2250 ON SUPELCOPORT
PROGRAM: 50°C FOR 4 MIN, 8°C/MIN TO 270°C
DETECTOR: MASS SPECTROMETER

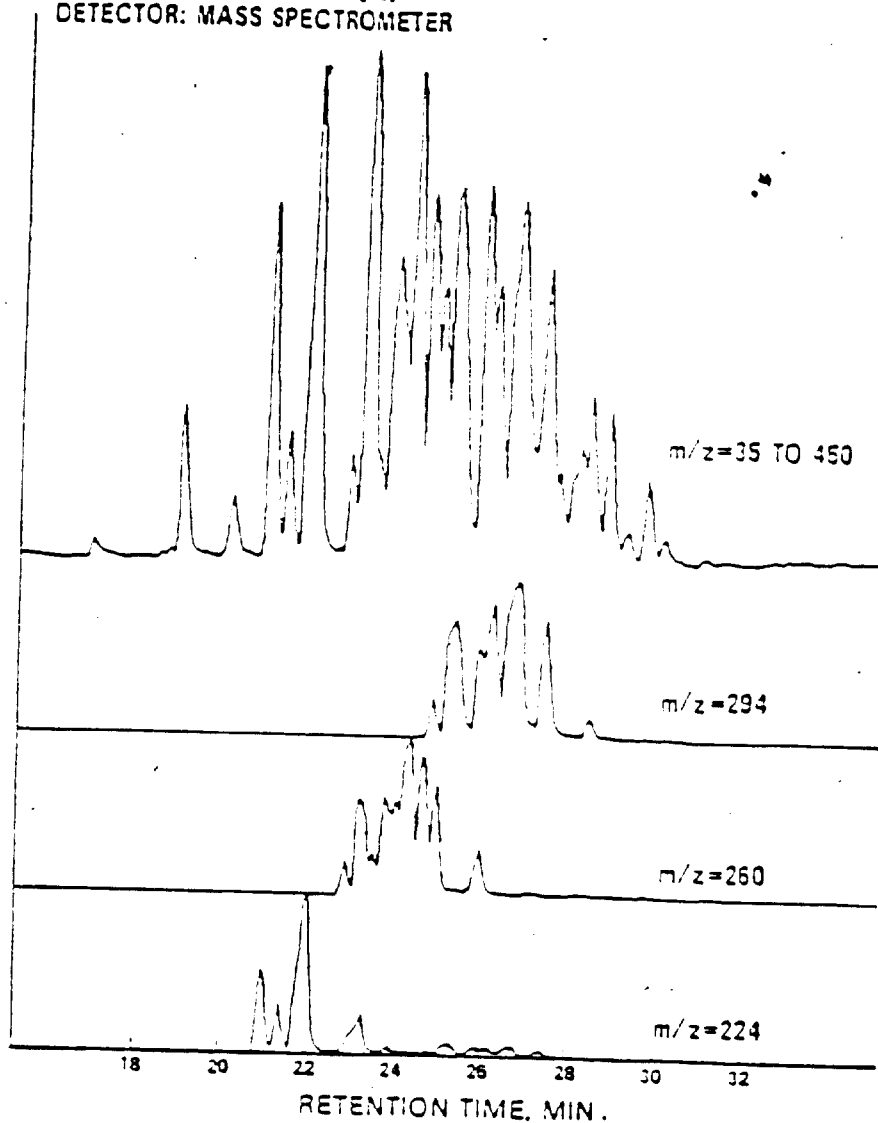


Figure 9. Gas chromatogram of PCB-1242.

COLUMN: 3% SP-2250 ON SUPELCOPORT
PROGRAM: 50°C FOR 4 MIN. 8°C/MIN TO 270°C
DETECTOR: MASS SPECTROMETER

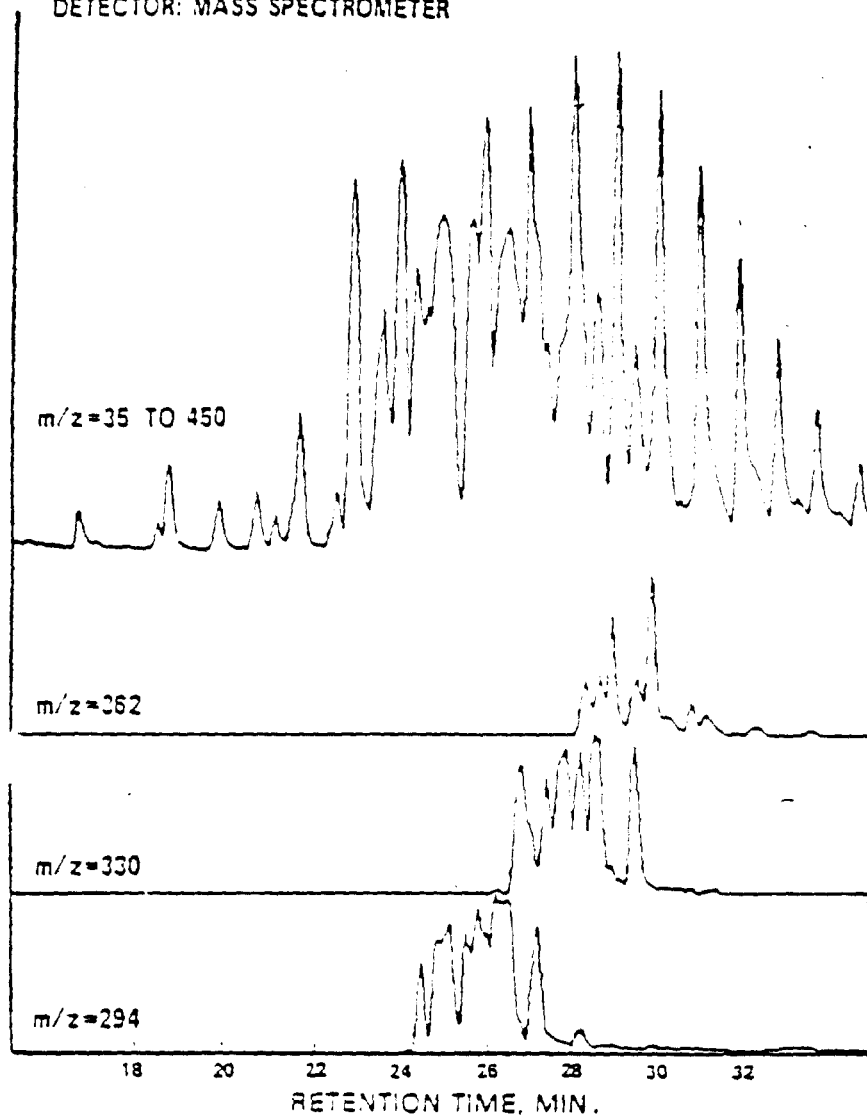


Figure 10. Gas chromatogram of PCB-1248.

COLUMN: 3% SP-2250 ON SUPELCOPORT
PROGRAM: 50°C FOR 4 MIN, 8°C/MIN TO 270°C
DETECTOR: MASS SPECTROMETER

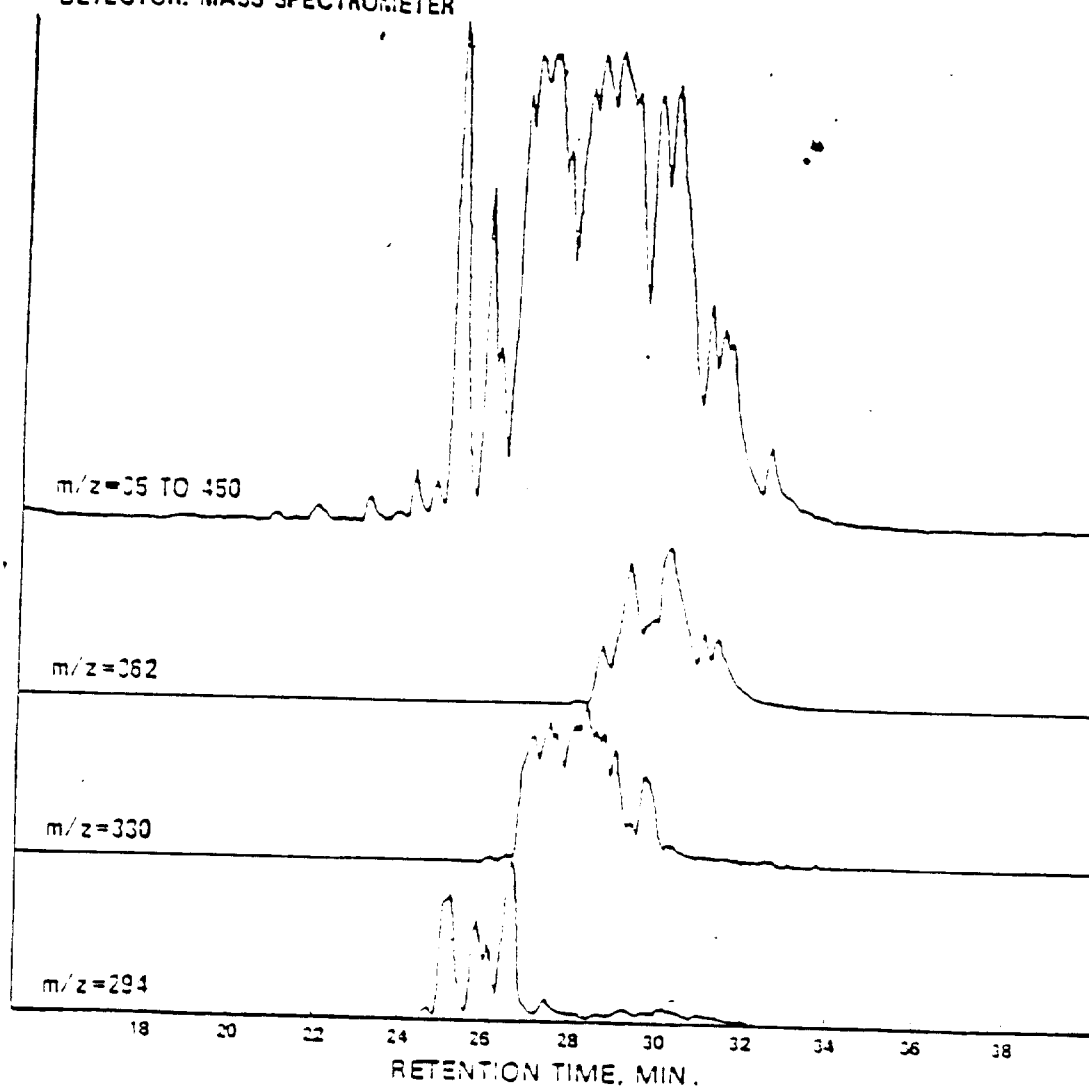


Figure 11. Gas chromatogram of PCB-1254.

COLUMN: 3% SP-2250 ON SUPELCOPORT
PROGRAM: 50°C FOR 4 MIN. 8°C/MIN TO 270°C
DETECTOR: MASS SPECTROMETER

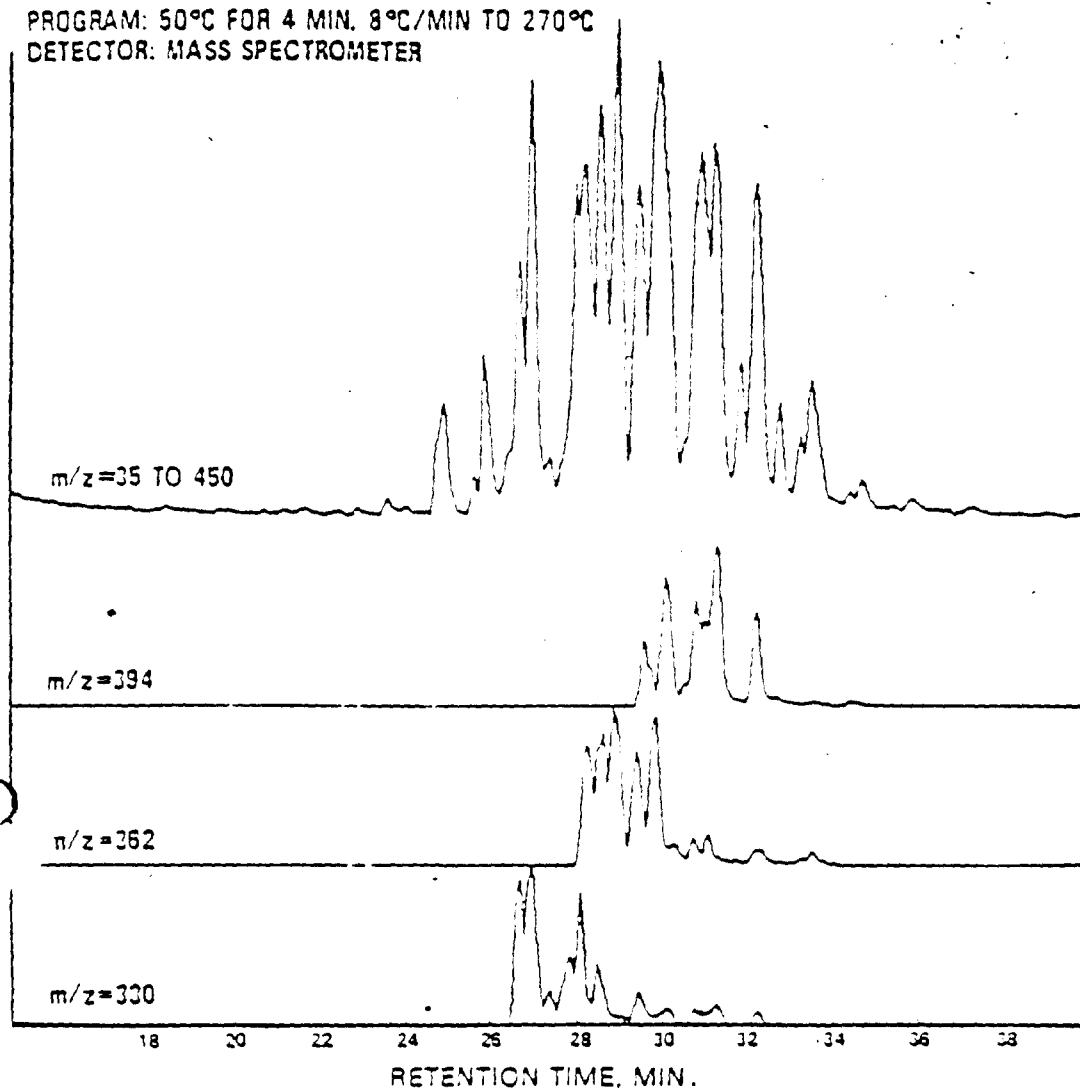
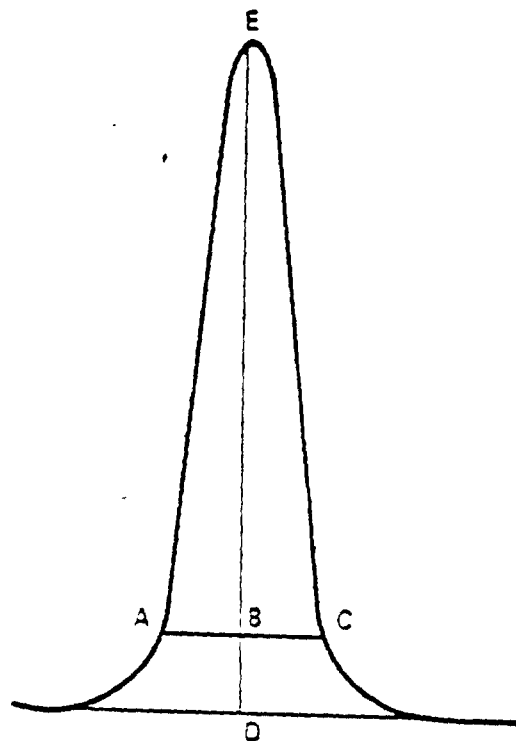


Figure 12. Gas chromatogram of PCB-1260.



$$\text{TAILING FACTOR} = \frac{BC}{AB}$$

Example calculation: Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

$$\text{Therefore: Tailing Factor} = \frac{12}{11} = 1.1$$

Figure 13. Tailing factor calculation.

STATE OF N.H. WATER POLLUTION CONTROL LABORATORY

STANDARD METHOD FOR DETERMINATION OF: Organochlorine Pesticides and
Polychlorinated Biphenyls
Federal Register, July 1, 1982, Method 608
Method 625

TECHNIQUE USED: Gas Chromatograph - Direct Injection
External Standard Techniques

A. Sampling Methodology:

1. Preservative: Storage at 4° C
2. Holding Time: 7 days before extraction (if pH has been adjusted to a range of 5-9), and 40 days after extraction.
3. Required Volume: 1000 mL
4. Container Type: Glass bottle with teflon seal on cap.

B. Techniques:

1. All samples are screened initially on a gas chromatograph.
2. If gas chromatography analysis yields a positive result for any of the polychlorinated biphenyls or organochlorine pesticides, then that sample will be confirmed and subsequently quantified on the GC/MS.
 - a. Confirmation - two confirmatory techniques will be employed for these compounds; initially, they will be screened by a selected ion monitoring profile, to insure proper sensitivity. As a secondary measure, they would be confirmed by the use of chemical ionization made of mass spectroscopy.
 - b. Quantitation - the method would be external standard, using two selected ions per compound.

C. Sample Preparation:

1. Extraction
 - a. Pour 1000 mL of sample into a 2000 mL separatory funnel.
 - b. Adjust the pH of sample to 7.0 pH units. If needed use either 1:1 sulfuric acid or 10N NaOH as required.
 - c. Add spikes and surrogates.
 - d. Add 60 mL of Methylene Chloride.
 - e. Shake the separatory funnel for 2 minutes, venting as needed.
 - f. If an emulsion is formed, add 50 mL of saturated salt solution and shake again for 2 minutes, venting as necessary.
 - g. Allow the organic layer to separate from the water phase for a minimum of 10 minutes.

STATE OF N.H. WATER POLLUTION CONTROL LABORATORY
STANDARD METHOD FOR DETERMINATION OF: Organochlorine Pesticides and
Polychlorinated Biphenyls

TECHNIQUE USED: Gas Chromatograph - Direct Injection
External Standard Techniques

- h. Collect the Methylene Chloride layer into a 500 mL evaporative flask with an attached 10 mL concentrator tube, a Kuderna-Danish (K-D) concentrator (Note: The concentrator tube should already contain an ebulator).
- i. Repeat steps d, e, g and h two times more so that the sample has been extracted a total of three times and the final volume of the extract is 120 mL.
- j. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete phase separation. This may include stirring, filtration of the emulsion through an anhydrous NaSO_4 column (10 cm), or centrifugation. If the NaSO_4 column is employed, it should be prewet with MeCl_2 and rinsed three times its volume with MeCl_2 , after the sample has passed through. This three volume rinse should be collected with the sample in the K-D concentrator apparatus.
- k. To the evaporative flask attach a three-ball Snyder column. Prewet the Snyder Column by adding about 1 mL of Methylene Chloride to the top of the column. Place the K-D apparatus on the hot water bath (set at medium, 80°C), so that the concentrator tube is partially immersed in hot water, and the entire lower rounded surface of the flask is bathed in hot vapor. At proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. Complete concentration, when the volume of liquid reaches 1 mL, should require only 15-20 minutes. Once concentrated, allow the sample to cool for 10 minutes.
- l. Rinse Snyder column with Methylene Chloride. Before removing, allow it to drain completely. The evaporative flask should be rinsed next and allowed to drain into concentrator tube before removing.
- m. Add a boiling chip to the concentrator tube and attach a micro Snyder Column. Place the apparatus on a tube concentrator, and take down to a volume of 1 mL, rinse down the Snyder Column with MeCl_2 and cool for 10 minutes. Reattach the micro evaporator flask.
- n. Increase the temperature of the hot water bath to about 98°C (high setting). Add 50 mL of hexane and a new boiling chip and reattach the three-balled Snyder Column. Prewet the column by adding 1 mL of hexane to the top of the column. Concentrate the solvent extract as before. When the volume of the liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool at least 10 minutes.

STATE OF N.H. WATER POLLUTION CONTROL LABORATORY

STANDARD METHOD FOR DETERMINATION OF: Organochlorine Pesticides and
Polychlorinated Biphenyls

TECHNIQUE USED: Gas Chromatograph - Direct Injection
External Standard Techniques

- o. Rinse and remove Synder column. Rinse and remove flask. Put the 10 mL concentrator tube on the tube heater with a micro Synder Column and bring down to a final volume of 1 mL after rinsing down the micro Synder Column (a 1 mL volumetric flask must be used for accuracy).
- p. Transfer to a 20 mL vial with a teflon cap properly labeled (Sample # , PCB and/or Organochloric Pesticides) and store in the freezer.

2. Cleanup and Separation

Reference: Federal Register, July 1, 1982, Method 608 (608-6)

NOTE: Only used on samples which could not be cleaned-up by methods previously mentioned.

D. Instrument Set-Up and Run:

1. Gas chromatographic screen for PCB's and organochlorine pesticides:

Column: 1.5% SP - 2250 and 1.95% SP - 2401 on Supelcoport

Detector: Electron capture

Reference: Federal Register, July 1, 1982, Method 608, (608-6, 608-11)

2. Gas chromatography/mass spectrometry for organochlorine pesticides and PCB's:

Reference: Federal Register, July 1, 1982, Method 625, (625-6, 625-13)

E. Data Handling Procedures:

1. Accuracy
 - a. % Recovery of the Q.C. spikes.
2. Precision
 - a. Duplicates
 - b. Standard curve linearity
3. Data Recording Procedure
 - a. The integration program (ESTD) is used to integrate the data (Hewlett Packard 1000, E series).
 - b. Hard copies of the integration are printed.
 - c. The data is then reviewed by the supervisor.
 - d. The data is then entered into the general laboratory computer for dissemination (Hewlett Packard 1000, E Series).
 - e. Samples and Q.C. results are handled identically.

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STATE OF N.H. WATER POLLUTION CONTROL LABORATORY
STANDARD METHOD FOR DETERMINATION OF: Organochlorine, Pesticides and
Polychlorinated Biphenyls

TECHNIQUE USED: Gas Chromatograph - Direct Injection
External Standard Techniques

F. Reagents:

Reference: Federal Register, July 1, 1982, Method 608, (608-3)

G. Quality Control - 20%:

1. Duplicates
One duplicate analyzed for each 5 samples.
2. Blanks
One blank analyzed for each group of samples.
3. Spike

EPA quality control sample analyzed for each group of samples (Both Organochlorine Pesticides and Polychlorinated Biphenyls). Samples are prepared according to the sheet received with the sample.

H. Washing:

All glassware used (i.e transfer pipettes, separatory funnels, etc.) are washed with hot water and detergent, rinsed well with DI water, and triple solvent rinsed: Acetone, Methylene Chloride and Hexane, in that order.

CND/pdl
(1848)

Method 608—Organochlorine Pesticides and PCBs

1. Scope and Application

1.1 This method covers the determination of certain organochlorine pesticides and PCBs. The following parameters can be determined by this method:

Parameter	STOREY No.	CAS No.
Aldrin	39330	508-00-2
δ-BHC	28337	319-84-6
β-BHC	39338	319-85-7
γ-BHC	34253	319-86-8
γ-BHC	39340	58-69-9
Chlordane	39350	57-74-9
4,4'-DDD	39310	72-54-8
4,4'-DDE	39320	72-55-9
4,4'-DDT	39300	50-29-3
Dieldrin	39380	60-57-1
Endosulfan I	34361	943-90-8
Endosulfan II	34356	33212-65-8
Endosulfan sulfate	34351	1031-37-4
Endrin	39390	72-20-8
Endrin aldehyde	34768	7421-93-4
Heptachlor	39410	75-44-8
Heptachlor epoxide	39420	1024-57-3
Toxaphene	39400	8001-35-2
PCB-1016	34671	2974-11-2
PCB-1221	39458	1104-28-2
PCB-1232	39432	11161-16-5
PCB-1242	39496	33469-21-9
PCB-1248	39500	2972-29-6
PCB-1254	39504	11097-69-1
PCB-1260	39508	11096-82-5

1.2 This is a gas chromatographic (GC) method applicable to the determination of the compounds listed above in municipal and industrial discharges as provided under 40 CFR 136.1. When this method is used to analyze unfamiliar samples for any or all of the compounds above, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the primary column. Method 625 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative and quantitative confirmation of results for all of the parameters listed above, using the extract produced by this method.

1.3 The method detection limit (MDL) defined in Section 14.1¹ for each parameter is listed in Table 1. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.4 The sample extraction and concentration steps in this method are essentially the same as in Methods 606, 609, 611, and 612. Thus, a single sample may be extracted to measure the parameters included in the scope of each of these methods. When cleanup is required, the concentration levels must be high enough to permit selecting aliquots, as necessary, to apply appropriate cleanup procedures. The analyst is allowed the latitude, under Section 12, to select chromatographic conditions appropriate for the simultaneous measurement of combinations of these parameters.

1.5 Any modification of this method, beyond those expressly permitted, shall be considered as a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. Summary of Method

2.1 A measured volume of sample, approximately 1-L, is extracted with methylene chloride using a separatory funnel. The methylene chloride extract is dried and exchanged to hexane during concentration to a volume of 10 mL or less. The extract is separated by gas chromatography and the parameters are then measured with an electron capture detector.²

2.2 The method provides a Florisil column cleanup procedure and an elemental sulfur removal procedure to aid in the elimination of interferences that may be encountered.

3. Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 3.1.1.

3.1.1 Glassware must be scrupulously cleaned.³ Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by detergent washing with hot water and rinses with tap water and distilled water. The glassware should then be drained dry and heated in a muffle furnace at 400 °C for 15 to 30 min. Some thermally stable materials, such as PCBs, may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Thorough rinsing with such solvents usually eliminates PCB interference.

Volumetric ware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences by phthalate esters can pose a major problem in pesticide analysis when using the electron capture detector. These compounds generally appear in the chromatogram as large late eluting peaks, especially in the 15 and 50% fractions from Florisil. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalates can best be

minimized by avoiding the use of plastics in the laboratory. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination.^{4,5} The interferences from phthalate esters can be avoided by using a microcoulometric or electrolytic conductivity detector.

3.3 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled. The cleanup procedures in Section 11 can be used to overcome many of these interferences, but unique samples may require additional cleanup approaches to achieve the MDL listed in Table 1.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified ** for the information of the analyst.

4.2 The following parameters covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens: 4,4'-DDT, 4,4'-DDD, the BHCs, and the PCBs. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

5. Apparatus and Materials

5.1 Sampling equipment for discrete or composite sampling.

5.1.1 Grab sample bottle—1-L or 1-qt. amber glass, fitted with a screw cap lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The bottle and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.1.2 Automatic sampler (optional)—The sampler must incorporate glass sample containers for the collection of a minimum of 250 mL of sample. Sample containers must be kept refrigerated at 4°C and protected from light during composting. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. Before use, however, the compressible tubing should be thoroughly rinsed with methanol, followed by repeated rinsings with distilled water to minimize the potential for contamination of the sample. An integrating

flow meter is required to collect flow proportional composites.

5.2. Glassware (All specifications are suggested. Catalog numbers are included for illustration only.):

5.2.1 Separatory funnel—2-L with Teflon stopcock.

5.2.2 Drying column—Chromatographic column, approximately 400 mm long × 19 mm ID, with coarse frit filter disc.

5.2.3 Chromatographic column—400 mm long × 22 mm ID, with Teflon stopcock and coarse frit filter disc (Kontes K-42054 or equivalent).

5.2.4 Concentrator tube, Kuderna-Danish—10-mL graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

5.2.5 Evaporative flask, Kuderna-Danish—500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

5.2.6 Snyder column, Kuderna-Danish—Three-bail macro (Kontes K-503000-0121 or equivalent).

5.2.7 Vials—10 to 15-mL, amber glass, with Teflon-lined screw cap.

5.3. Boiling chips—Approximately 10/40 mesh. Heat to 400°C for 30 min or Soxhlet extract with methylene chloride.

5.4. Water bath—Heated, with concentric ring cover, capable of temperature control ($\pm 2^\circ\text{C}$). The bath should be used in a hood.

5.5. Balance—Analytical, capable of accurately weighing 0.0001 g.

5.6. Gas chromatograph—An analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder. A data system is recommended for measuring peak areas.

5.6.1 Column 1—1.8 m long × 4 mm ID glass, packed with 1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 mesh) or equivalent. This column was used to develop the method performance statements in Section 14. Guidelines for the use of alternate column packings are provided in Section 12.1.

5.6.2 Column 2—1.8 m long × 4 mm ID glass, packed with 3% OV-1 on Supelcoport (100/120 mesh) or equivalent.

5.6.3 Detector—Electron capture detector. This detector has proven effective in the analysis of wastewaters for the parameters listed in the scope (Section 1.1), and was used to develop the method performance statements in Section 14. Guidelines for the use of alternate detectors are provided in Section 12.1.

6. Reagents

6.1 Reagent water—Reagent water is defined as a water in which an interferent is not observed at the MDL of the parameters of interest.

6.2 Sodium hydroxide solution (10 N)—Dissolve 40 g of NaOH (ACS) in reagent water and dilute to 100 mL.

6.3 Sodium thiosulfate—ACS Granular.

6.4 Sulfuric acid (1-1)—Slowly, add 50 mL to H₂SO₄ (ACS, sp. gr. 1.84) to 50 mL of reagent water.

6.5 Acetone, hexane, isooctane, methylene chloride—Pesticide quality or equivalent.

6.6 Ethyl ether—Nanograde, redistilled in glass if necessary.

6.6.1 Ethyl ether must be shown to be free of peroxides before it is used as indicated by EM Laboratories Quant test strips. (Available from Scientific Products Co., Cat. No. P1128-8, and other suppliers.)

6.6.2 Procedures recommended for removal of peroxides are provided with the test strips. After cleanup, 20 mL of ethyl alcohol preservative must be added to each liter of ether.

6.7 Sodium sulfate—ACS Granular, anhydrous. Purify by heating at 400°C for 4 h in a shallow tray.

6.8 Florisil—PR grade (60/100 mesh). Purchase activated at 1250°F and store in the dark in glass containers with ground glass stoppers or foil-lined screw caps. Before use, activate each batch at least 18 h at 130°C in a foil-covered glass container and allow to cool.

6.9 Mercury—Triple distilled.

6.10 Copper powder—Activated.

6.11 Stock standard solutions (1.00 µg/µL)—Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

6.11.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in isooctane and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 95% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

6.11.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.11.3 Stock standard solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

6.12 Quality control check sample concentrate—See Section 8.2.1.

7. Calibration

7.1 Establish gas chromatographic operating conditions equivalent to those given in Table 1. The gas chromatographic system can be calibrated using the external standard technique (Section 7.2) or the internal standard technique (Section 7.3).

7.2 External standard calibration procedure:

7.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with isooctane. One of the external standards should be at a concentration near, but above, the MDL (Table 1), and the other concentrations should correspond to the

expected range of concentrations found in real samples or should define the working range of the detector.

7.2.2 Using injections of 2 to 5 µL, analyze each calibration standard according to Section 12 and tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each compound. Alternatively, the ratio of response to amount injected (calibration factor) is a constant over the working range ($< 10\%$ relative standard deviation, RSD), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of calibration curve.

7.3 Internal standard calibration procedure—To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

7.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volume of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards, and dilute volume with isooctane. One of the standards should be at a concentration near, but above, the MDL and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.3.2 Using injections of 2 to 5 µL, analyze each calibration standard according to Section 12 and tabulate peak height or area responses against concentration for each compound and internal standard. Calculate response factors (RF) for each compound using Equation 1.

Equation 1.

$$RF = \frac{(A_p)(C_{is})}{(A_{is})(C_p)}$$

where:

A_p = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard (µg/L).

C_p = Concentration of the parameter to be measured (µg/L).

If the RF value over the working range is a constant ($< 10\%$ RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_p/A_{is} , vs. RF.

7.4 The working calibration curve, calibration factor, or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than $\pm 15\%$, the test must be repeated using a fresh calibration

standard. Alternatively, a new calibration curve must be prepared for that compound.

7.5 The cleanup procedure in Section 11 utilizes Florisil column chromatography. Florisil from different batches or sources may vary in adsorptive capacity. To standardize the amount of Florisil which is used, the use of lauric acid value* is suggested. The referenced procedure determines the adsorption from hexane solution of lauric acid (mg) per g of Florisil. The amount of Florisil to be used for each column is calculated by dividing 110 by this ratio and multiplying by 20 g.

7.6 Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.1.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Sections 10.4, 11.1, and 12.1) to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 Before processing any samples, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system and glassware are under control. Each time a set of samples is extracted or reagents are changed, a reagent water blank must be processed as a safeguard against laboratory contamination.

8.1.4 The laboratory must, on an ongoing basis, spike and analyze a minimum of 10% of all samples to monitor and evaluate laboratory data quality. This procedure is described in Section 8.3.

8.1.5 The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 8.4. The frequency of the check standard analyses is equivalent to 10% of all samples analyzed but may be reduced if spike recoveries from samples (Section 8.3) meet all specified quality control criteria.

8.1.6 The laboratory must maintain performance records to document the quality

of data that is generated. This procedure is described in Section 8.5.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 A quality control (QC) check sample concentrate is required containing each single-component parameter of interest at the following concentrations in acetone: 6,6'-DDD, 10 µg/mL; 4,4'-DDT, 10 µg/mL; endosulfan II, 10 µg/mL; endosulfan sulfate, 10 µg/mL; endrin, 10 µg/mL; any other single-component pesticide, 2 µg/mL. If this method is only to be used to analyze for PCBs, chlordane, or toxaphene, the QC check sample concentrate should contain the most representative multicomponent parameter at a concentration of 50 µg/mL in acetone. The QC check sample concentrate must be obtained from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory in Cincinnati, Ohio, if available. If not available from that source, the QC check sample concentrate must be obtained from another external source. If not available from either source above, the QC check sample concentrate must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

8.2.2 Using a pipet, prepare QC check samples at the test concentrations shown in Table 3 by adding 1.00 mL of QC check sample concentrate to each of four 1-L aliquots of reagent water.

8.2.3 Analyze the well-mixed QC check samples according to the method beginning in Section 10.

8.2.4 Calculate the average recovery (\bar{X}) in µg/mL and the standard deviation of the recovery (S) in µg/mL for each parameter using the four results.

8.2.5 For each parameter compare \bar{X} and S with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 3. If \bar{X} and S for all parameters of interest meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual \bar{X} exceeds the precision limit or any individual S falls outside the range for accuracy, the system performance is unacceptable for that parameter.

Note.—The large number of parameters in Table 3 present a substantial probability that one or more will fail at least one of the acceptance criteria when all parameters are analyzed.

8.2.6 When one or more of the parameters tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 8.2.6.1 or 8.2.6.2.

8.2.6.1 Locate and correct the source of the problem and repeat the test for all parameters of interest beginning with Section 8.2.2.

8.2.6.2 Beginning with Section 8.2.2, repeat the test only for those parameters that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.2.2.

8.3 The laboratory must, on an ongoing basis, spike at least 10% of the samples from

each sample site being monitored to assess accuracy. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.3.1 The concentration of the spike in the sample should be determined as follows:

8.3.1.1 If, as in compliance monitoring, the concentration of a specific parameter in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.2 If the concentration of a specific parameter in the sample is not being checked against a limit specific to that parameter, the spike should be at the test concentration in Section 8.2.2 or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.3 If it is impractical to determine background levels before spiking (e.g., maximum holding times will be exceeded), the spike concentration should be (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or the test concentration in Section 8.2.2.

8.3.2 Analyze one sample aliquot to determine the background concentration (B) of each parameter. If necessary, prepare a new QC check sample concentrate (Section 8.2.1) appropriate for the background concentrations in the sample. Spike a second sample aliquot with 1.0 mL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each parameter. Calculate each percent recovery (P) as $100(A-B)/T$, where T is the known true value of the spike.

8.3.3 Compare the percent recovery (P) for each parameter with the corresponding QC acceptance criteria found in Table 3. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1.¹⁰ If spiking was performed at a concentration lower than the test concentration in Section 8.2.2, the analyst must use either the QC acceptance criteria in Table 3, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of a parameter: (1) Calculate accuracy (\bar{X}) using the equation in Table 4, substituting the spike concentration (T) for C ; (2) calculate overall precision (S) using the equation in Table 4, substituting \bar{X} for \bar{X} ; (3) calculate the range for recovery at the spike concentration as $100(\bar{X}/T) \pm 2.44(100 S/T)^{1/2}$.

8.3.4 If any individual P falls outside the designated range for recovery, that parameter has failed the acceptance criteria. A check standard containing each parameter that failed the criteria must be analyzed as described in Section 8.4.

8.4 If any parameter fails the acceptance criteria for recovery in Section 8.3, a QC

check standard containing each parameter that failed must be prepared and analyzed.

Note.—The frequency for the required analysis of a QC check standard will depend upon the number of parameters being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of parameters in Table 3 must be measured in the sample in Section 8.3, the probability that the analysis of a QC check standard will be required is high. In this case the QC check standard should be routinely analyzed with the spike sample.

8.4.1 Prepare the QC check standard by adding 1.0 mL of QC check sample concentrate (Sections 8.2.1 or 8.3.2) to 1 L of reagent water. The QC check standard needs only to contain the parameters that failed criteria in the test in Section 8.3.

8.4.2 Analyze the QC check standards to determine the concentration measured (A) of each parameter. Calculate each percent recovery (P_r) as $100 (A/T)\%$, where T is the true value of the standard concentration.

8.4.3 Compare the percent recovery (P_r) for each parameter with the corresponding QC acceptance criteria found in Table 3. Only parameters that failed the test in Section 8.3 need to be compared with these criteria. If the recovery of any such parameter falls outside the designated range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.5 As part of the QC program for the laboratory, method accuracy for wastewater samples must be assessed and records must be maintained. After the analysis of five spiked wastewater samples as in Section 8.3, calculate the average percent recovery (\bar{P}) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $\bar{P} - 2s_p$ to $\bar{P} + 2s_p$. If $\bar{P} = 90\%$ and $s_p = 10\%$, for example, the accuracy interval is expressed as 70–110%. Update the accuracy assessment for each parameter on a regular basis (e.g., after each five to ten new accuracy measurements).

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or mass spectrometer must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 Grab samples must be collected in glass containers. Conventional sampling practices¹¹ should be followed, except that

the bottle must not be prerinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of Tygon tubing and other potential sources of contamination.

9.2 All samples must be iced or refrigerated at 4 °C from the time of collection until extraction. If the samples will not be extracted within 72 h of collection, the sample should be adjusted to a pH range of 5.0 to 9.0 with sodium hydroxide solution or sulfuric acid. Record the volume of acid or base used. If aidrin is to be determined, add sodium thiosulfate when residual chlorine is present. EPA Methods 330.4 and 330.5 may be used for measurement of residual chlorine.¹² Field test kits are available for this purpose.

9.3 All samples must be extracted within 7 days of collection and completely analyzed within 40 days of extraction.¹³

10. Sample Extraction

10.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2-L separatory funnel.

10.2 Add 60 mL of methylene chloride to the sample bottle, seal, and shake 30 s to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 250-mL Erlenmeyer flask.

10.3 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

10.4 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D concentrator if the requirements of Section 8.2 are met.

10.5 Pour the combined extract through a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

10.6 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (60 to 85 °C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus

and the water temperature as required to complete the concentration in 15 to 20 min. At the proper rate of distillation the balls of column will actively chatter but the chamber will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

10.7 Increase the temperature of the water bath to about 80 °C. Momentarily remove the Snyder column, add 50 mL of hexane and a new boiling chip, and reattach the Snyder column. Concentrate the extract as in Section 10.6, except use hexane to prewet the column. The elapsed time of concentration should be 5 to 10 min.

10.8 Remove the Snyder column and the flask and its lower joint into the concentrator tube with 1 to 2 mL of hexane. A 5-mL syringe is recommended for this operation. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial. If the sample extract requires no further cleanup, proceed with gas chromatographic analysis (Section 12). If the sample requires further cleanup, proceed to Section 11.

10.9 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11. Cleanup and Separation

11.1 Cleanup procedures may not be necessary for a relatively clean sample matrix. If particular circumstances demand the use of a cleanup procedure, the analyst may use either procedure below or any other appropriate procedure. However, the analyst first must demonstrate that the requirements of Section 8.2 can be met using the method revised to incorporate the cleanup procedure. The Florisil column allows for a select fractionation of the compounds and will eliminate polar interferences. Elemental sulfur, which interferes with the electron capture gas chromatography of certain pesticides, can be removed by the technique described in Section 11.3.

11.2 Florisil column cleanup:

11.2.1 Place a weight of Florisil (nominal 20 g) predetermined by calibration (Section 7.5), into a chromatographic column. Tap the column to settle the Florisil and add 1 to 2 cm of anhydrous sodium sulfate to the top.

11.2.2 Add 60 mL of hexane to wet and rinse the sodium sulfate and Florisil. Just prior to exposure of the sodium sulfate layer to the air, stop the elution of the hexane by closing the stopcock on the chromatographic column. Discard the eluate.

11.2.3 Adjust the sample extract volume to 10 mL with hexane and transfer it from the K-D concentrator tube onto the column. Rinse the tube twice with 1 to 2 mL of hexane, adding each rinse to the column.

11.2.4 Place a 500-mL K-D flask and clean concentrator tube under the chromatographic column. Drain the column into the flask until the sodium sulfate layer is nearly exposed. Elute the column with 200 mL of 9% ethyl ether in hexane (V/V) (Fraction 1) at a rate of

about 5 mL/min. Remove the K-D flask and set it aside for later concentration. Elute the column again, using 200 mL of 15% ethyl ether in hexane (V/V) (Fraction 2), into a second K-D flask. Perform the third elution using 200 mL of 50% ethyl ether in hexane (V/V) (Fraction 3). The elution patterns for the pesticides and PCBs are shown in Table 2.

11.2.5 Concentrate the fractions as in Section 10.6, except use hexane to prewet the column and set the water bath at about 85 °C. When the apparatus is cool, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with hexane. Adjust the volume of each fraction to 10 mL with hexane and analyze by gas chromatography (Section 12).

11.3 Elemental sulfur will usually elute entirely in Fraction 1 of the Florsil column cleanup. To remove sulfur interference from this fraction or the original extract, pipet 1.00 mL of the concentrated extract into a clean concentrator tube or Teflon-sealed vial. Add one to three drops of mercury and seal.¹⁸ Agitate the contents of the vial for 15 to 30 s. Prolonged shaking (2 h) may be required. If so, this may be accomplished with a reciprocal shaker. Alternatively, activated copper powder may be used for sulfur removal.¹⁹ Analyze by gas chromatography.

12. Gas Chromatography

12.1 Table 1 summarizes the recommended operating conditions for the gas chromatograph. Included in this table are retention times and MDL that can be achieved under these conditions. Examples of the separations achieved by Column 1 are shown in Figures 1 to 10. Other packed or capillary (open-tubular) columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.2 are met.

12.2 Calibrate the system daily as described in Section 7.

12.3 If the internal standard calibration procedure is being used, the internal standard must be added to the sample extract and mixed thoroughly immediately before injection into the gas chromatograph.

12.4 Inject 2 to 5 µL of the sample extract or standard into the gas chromatograph using the solvent-rush technique.¹⁸ Smaller (1.0 µL) volumes may be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 µL, the total extract volume, and the resulting peak size in area or peak height units.

12.5 Identify the parameters in the sample by comparing the retention times of the peaks in the sample chromatogram with those of the peaks in standard chromatograms. The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

12.6 If the response for a peak exceeds the working range of the system, dilute the extract and reanalyze.

12.7 If the measurement of the peak response is prevented by the presence of interferences, further cleanup is required.

13. Calculations

13.1 Determine the concentration of individual compounds in the sample.

13.1.1 If the external standard calibration procedure is used, calculate the amount of material injected from the peak response using the calibration curve or calibration factor determined in Section 7.2.2. The concentration in the sample can be calculated from Equation 2.

Equation 2.

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A)(V_i)}{(V_s)(V_e)}$$

where:

A = Amount of material injected (ng).

V_i = Volume of extract injected (µL).

V_s = Volume of total extract (µL).

V_e = Volume of water extracted (mL).

13.1.2 If the internal standard calibration procedure is used, calculate the concentration in the sample using the response factor (RF) determined in Section 7.3.2 and Equation 3.

Equation 3.

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A_s)(L_i)}{(A_u)(RF)(V_e)}$$

where:

A_s = Response for the parameter to be measured.

A_u = Response for the internal standard.

L_i = Amount of internal standard added to each extract (µg).

V_e = Volume of water extracted (L).

13.2 When it is apparent that two or more PCB (Aroclor) mixtures are present, the Webb and McCall procedure¹⁸ may be used to identify and quantify the Aroclors.

13.3 For multicomponent mixtures (chlordane, toxaphene, and PCBs) match retention times of peaks in the standards with peaks in the sample. Quantitate every identifiable peak unless interference with individual peaks persist after cleanup. Add peak height or peak area of each identified peak in the chromatogram. Calculate as total response in the sample versus total response in the standard.

13.4 Report results in µg/L without correction for recovery data. All QC data obtained should be reported with the sample results.

14. Method Performance

14.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.¹ The MDL concentrations listed in Table 1 were obtained using reagent water.¹⁷ Similar results were achieved using

representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

14.2 This method has been tested for linearity of spike recovery from reagent water and has been demonstrated to be applicable over the concentration range from 4 × MDL to 1000 × MDL with the following exceptions: Chlordane recovery at 4 × MDL was low (60%); Toxaphene recovery was demonstrated linear over the range of 10 × MDL to 1000 × MDL.¹⁷

14.3 This method was tested by 20 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations.¹⁴ Concentrations used in the study ranged from 0.5 to 30 µg/L for single-component pesticide and from 8.5 to 400 µg/L for multicomponent parameters. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 4.

References

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TABLE 1.—CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS

Parameter	Retention time (min)		Method detection limit (ug/L)
	Col. 1	Col. 2	
a-BHC	1.35	1.52	0.003
γ-BHC	1.70	2.12	0.00
β-BHC	1.90	1.97	0.00
Heptachlor	2.00	3.35	0.003
δ-BHC	2.15	2.20	0.008
Aldrin	2.40	4.10	0.004
Heptachlor epoxide	3.50	5.00	0.083
Endosulfan I	4.50	6.20	0.014
4,4'-DDE	5.13	7.15	0.004
Endrin	5.45	7.23	0.002
4,4'-DDD	6.55	9.10	0.006
Endosulfan II	7.93	9.08	0.011
4,4'-DDT	8.00	6.28	0.004
Endrin aldehyde	9.40	11.75	0.012
Endosulfan sulfate	11.82	9.30	0.023
Chlordane	14.22	10.70	0.066
Toraphene	nr	nr	0.014
PCB-1018	nr	nr	0.24
PCB-1221	nr	nr	nr
PCB-1222	nr	nr	nr

TABLE 1.—CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS—Continued

Parameter	Retention time (min)		Method detection limit (ug/L)
	Col. 1	Col. 2	
PCB-1242	nr	nr	0.055
PCB-1248	nr	nr	nr
PCB-1254	nr	nr	nr
PCB-1250	nr	nr	nr

Column 1 conditions: Supelcoport (100/120 mesh) coated with 1.5% SP-2250/1.5% SP-2401 packed in a 1.8 m long x 4 mm ID glass column with 5% methane/95% argon carrier gas at 50 mL/min flow rate. Column temperature held isothermal at 200 °C, except for PCB-1018 through PCB-1248 should be measured at 150 °C.

Column 2 conditions: Supelcoport (100/120 mesh) coated with 3% OV-1 packed in a 1.8 m long x 4 mm ID glass column with 5% methane/95% argon carrier gas at 50 mL/min flow rate. Column temperature held isothermal at 200 °C for the peak det. at 140 °C for PCB-1221 and 1232, and at 170 °C for PCB-1018 and 1242 to 1250.

nr = Multiple peak response. See Figures 2 thru 10.

nd = Not determined.

TABLE 2.—DISTRIBUTION OF CHLORINATED PESTICIDES AND PCBs INTO FLORISIL COLUMN FRACTIONS

Parameter	Percent recovery by fraction		
	1	2	3
Aldrin	100		
a-BHC	100		
β-BHC	97		
δ-BHC	36		
γ-BHC	100		
Chlordane	100		
4,4'-DDD	99		
4,4'-DDE	36		
4,4'-DDT	100		
Endrin	0	100	
Endosulfan I	37	54	
Endosulfan II	0	31	
Endosulfan sulfate	0	108	
Endrin	4	36	
Endrin aldehyde	0	58	28
Heptachlor	100		
Heptachlor epoxide	100		
Toraphene	46		
PCB-1018	97		
PCB-1221	97		
PCB-1232	95	4	
PCB-1242	97		
PCB-1248	103		
PCB-1254	30		
PCB-1250	35		

* Eluent composition:

Fraction 1—5% ethyl ether in hexane.
Fraction 2—15% ethyl ether in hexane.
Fraction 3—50% ethyl ether in hexane.

TABLE 3.—QC ACCEPTANCE CRITERIA—METHOD 608

Parameter	Test conc. (ug/L)	Limit for S (ug/L)	Range for X (ug/L)	Range for P (ug/L)
Aldrin	2.0	0.42	1.08-2.24	42-122
a-BHC	2.0	0.48	36-2.44	37-134
β-BHC	2.0	0.84	0.78-2.50	17-147
δ-BHC	2.0	0.72	1.01-2.37	19-140
γ-BHC	2.0	0.48	0.88-2.32	32-127
Chlordane	50	10.0	27.5-54.3	45-119
4,4'-DDD	10	2.8	4.8-12.5	31-141
4,4'-DDE	2.0	0.55	1.08-2.50	30-145

TABLE 3.—QC ACCEPTANCE CRITERIA—METHOD 608—Continued

Parameter	Test conc. (ug/L)	Limit for S (ug/L)	Range for X (ug/L)
4,4'-DDT	10	3.8	4.8-13.7
Endrin	2.0	0.78	1.15-2.48
Endosulfan I	2.0	0.48	1.14-2.82
Endosulfan II	10	8.1	2.2-17.1
Endosulfan sulfate	10	2.7	3.8-13.2
Endrin	10	3.7	5.7-12.6
Heptachlor	2.0	0.40	0.88-2.00
Heptachlor epoxide	2.0	0.41	1.13-2.63
Toraphene	50	12.7	27.8-55.8
PCB-1018	50	10.0	30.5-51.5
PCB-1221	50	24.4	22.1-75.2
PCB-1222	50	17.9	14.0-58.5
PCB-1242	50	12.2	24.5-69.6
PCB-1248	50	15.9	29.0-70.2
PCB-1254	50	13.8	22.2-57.9
PCB-1250	50	10.4	18.7-54.9

S = Standard deviation of four recovery measurements (Section 8.2.4).

X = Average recovery for four recovery measurements (Section 8.2.4).

P = Percent recovery measured (Section 8.2.4).

0 = Detected; result must be greater than zero.

Note: These criteria are based directly upon the performance data in Table 4. Where necessary, the recovery have been broadened to assure applicability limits to concentrations below those used to develop the criteria.

TABLE 4. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION—METHOD 608

Parameter	Accuracy, as recovery, % (ug/L)	Single analysis precision, % (ug/L)	Over precision, % (ug/L)
Aldrin	0.81C-0.34	0.16X-0.34	0.20Z-0.34
a-BHC	0.94C-0.33	0.13X-0.34	0.23X-0.34
β-BHC	0.81C-0.37	0.22X-0.32	0.33X-0.37
δ-BHC	0.81C-0.37	0.19X-0.35	0.25X-0.37
γ-BHC	0.82C-0.38	0.12X-0.38	0.22X-0.38
Chlordane	0.82C-0.34	0.13X-0.13	0.19X-0.34
4,4'-DDD	0.84C-0.30	0.20X-0.18	0.27X-0.30
4,4'-DDE	0.85C-0.14	0.13X-0.38	0.28X-0.38
4,4'-DDT	0.93C-0.13	0.17X-0.39	0.31X-0.39
Endrin	0.90C-0.02	0.12X-0.19	0.18X-0.19
Endosulfan I	0.97C-0.34	0.10X-0.07	0.18X-0.34
Endosulfan II	0.93C-0.34	0.41X-0.88	0.47X-0.88
Endosulfan sulfate	0.89C-0.37	0.13X-0.33	0.24X-0.37
Endrin	0.89C-0.34	0.20X-0.25	0.24X-0.34
Heptachlor	0.89C-0.34	0.08X-0.13	0.16X-0.34
Heptachlor epoxide	0.89C-0.10	0.18X-0.11	0.25X-0.34
Toraphene	0.80C-1.74	0.09X-0.20	0.20X-0.34
PCB-1018	0.81C-0.50	0.13X-0.15	0.15X-0.50
PCB-1221	0.96C-0.85	0.29X-0.78	0.35X-0.85
PCB-1222	0.91C-10.79	0.21X-1.93	0.31X-3.01
PCB-1242	0.93C-0.70	0.11X-1.40	0.21X-1.40
PCB-1248	0.97C-1.08	0.17X-0.41	0.25X-0.41
PCB-1254	0.78C-2.07	0.15X-1.58	0.17X-2.07
PCB-1250	0.56C-3.15	0.22X-2.37	0.39X-4.44

X = Expected recovery for one of more measurements.

Z = Sample containing a concentration of C in ug/L.

S = Expected single analysis standard deviation of measurements at an average concentration found of X in ug/L.

X = Expected interlaboratory standard deviation of measurements at an average concentration found of X in ug/L.

C = Test value for the concentration in ug/L.

X = Average recovery found for measurements of samples containing a concentration of C in ug/L.

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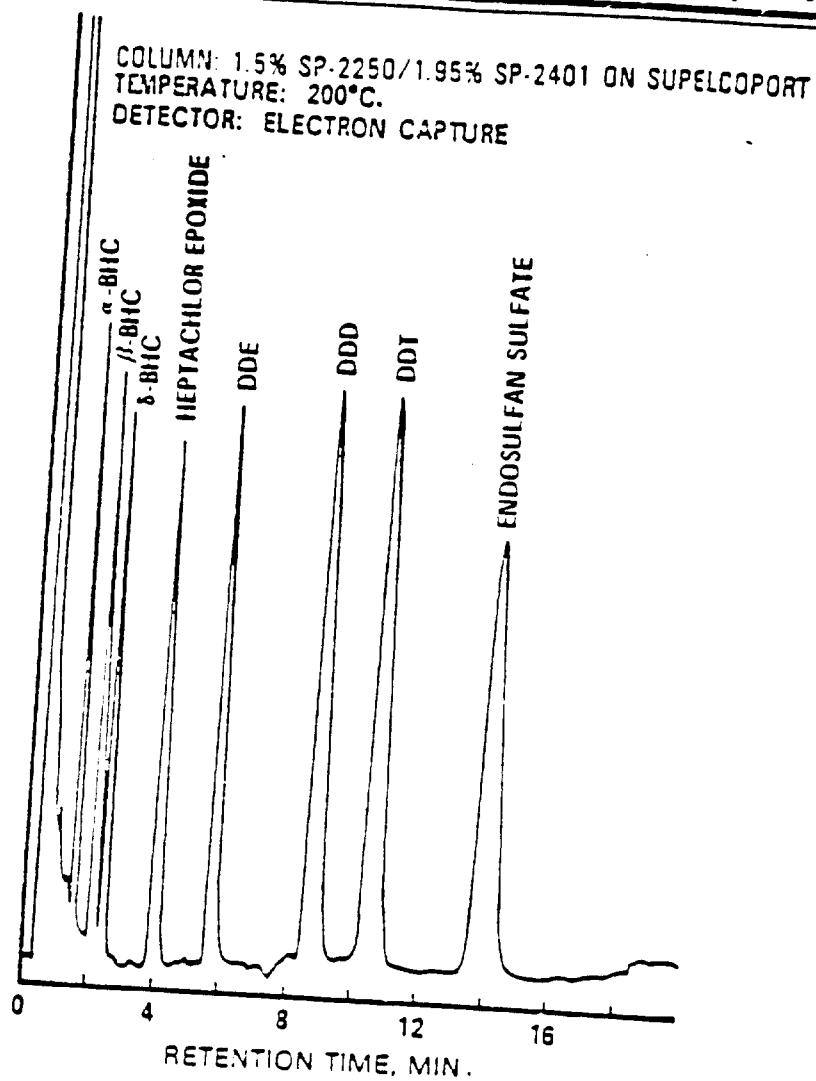


Figure 1. Gas chromatogram of pesticides.

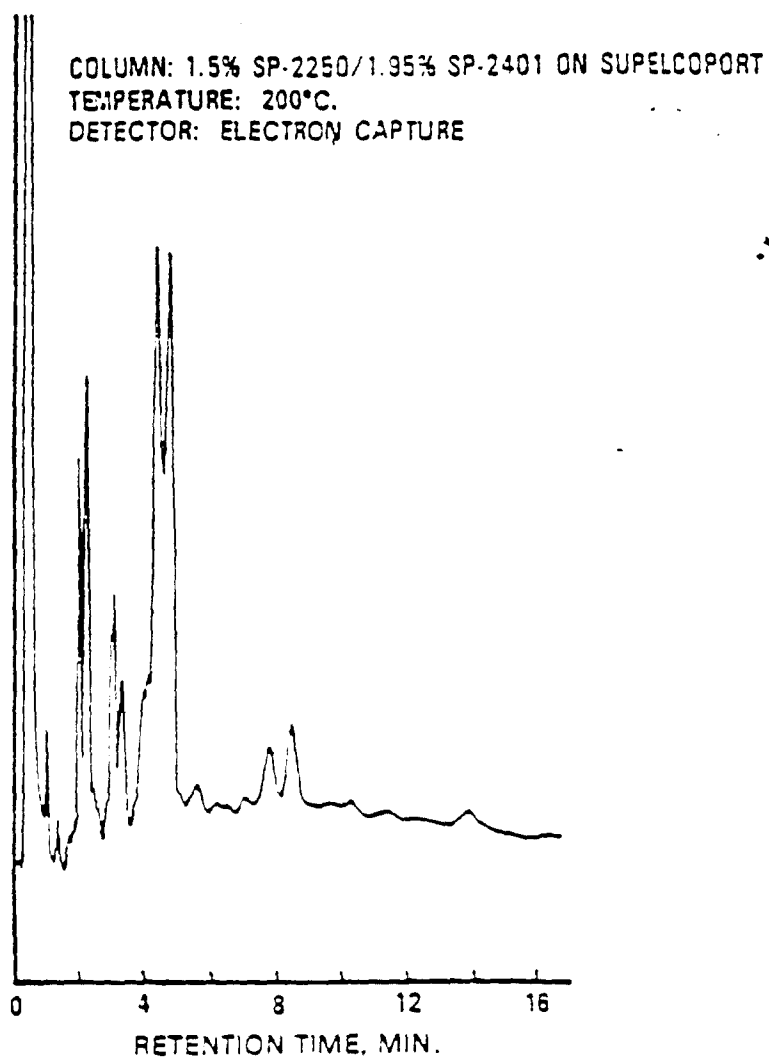


Figure 2. Gas chromatogram of chlordane.

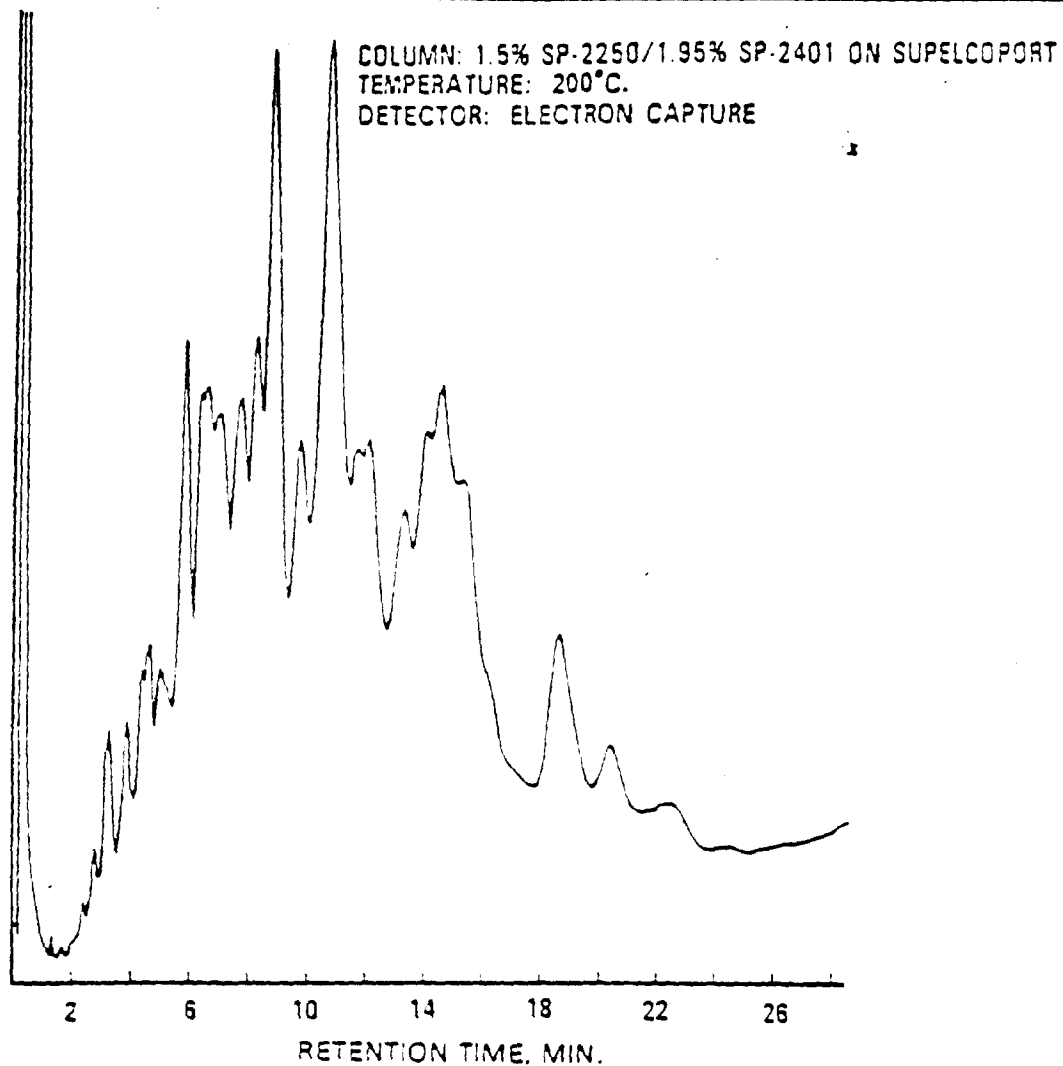


Figure 3. Gas chromatogram of toxaphene.

COLUMN: 1.5% SP-2250/1.95% SP-2401 ON SUPELCOPORT
TEMPERATURE: 160°C.
DETECTOR: ELECTRON CAPTURE

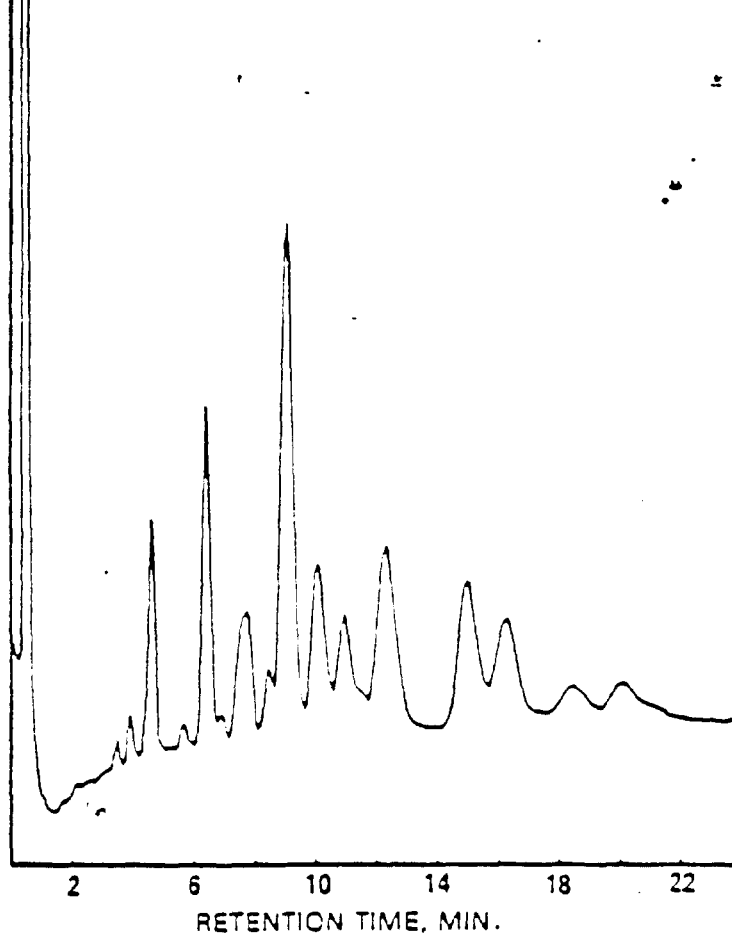


Figure 4. Gas chromatogram of PCB-1016.

C
COLUMN: 1.5% SP-2250/1.95% SP-2401 ON SUPELCOPORT
TEMPERATURE: 160°C.
DETECTOR: ELECTRON CAPTURE

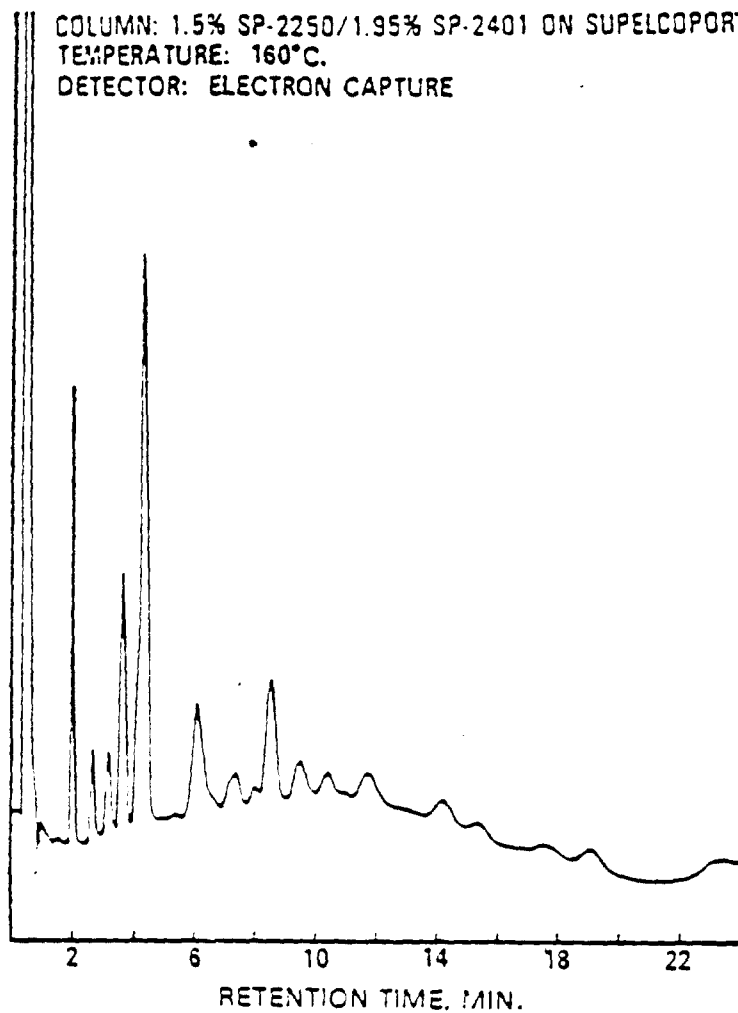


Figure 5. Gas chromatogram of PCB-1221.

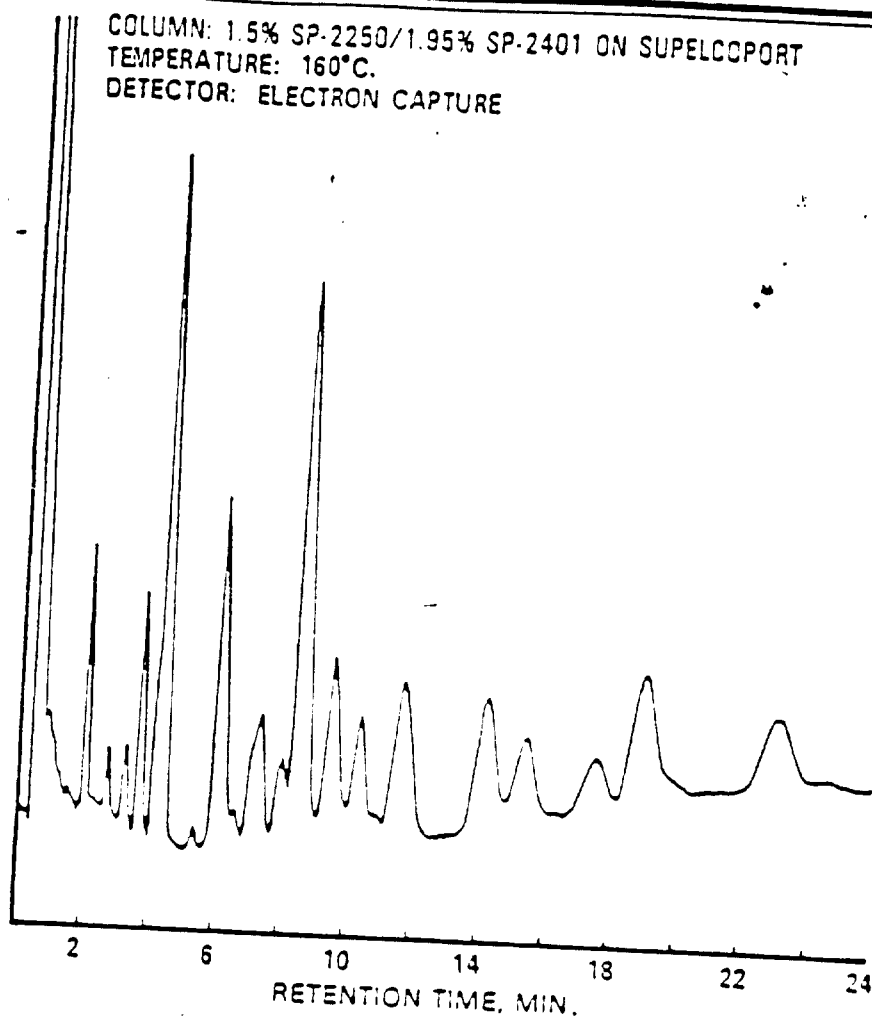


Figure 6. Gas chromatogram of PCB-1232.

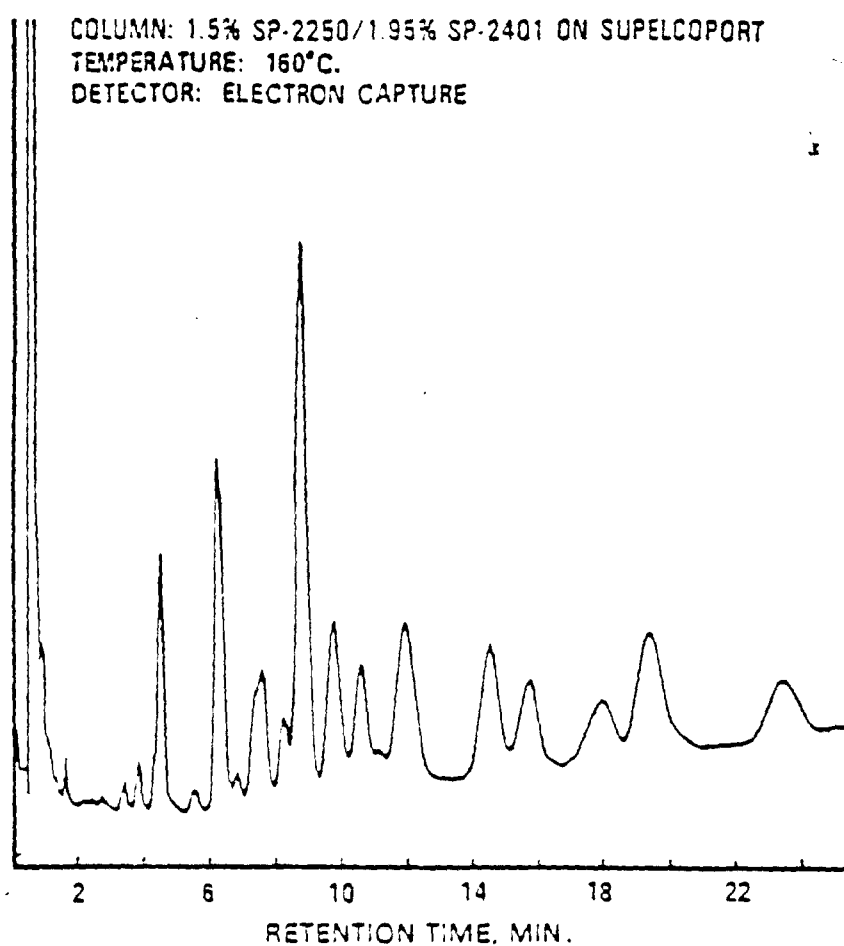


Figure 7. Gas chromatogram of PCB-1242.

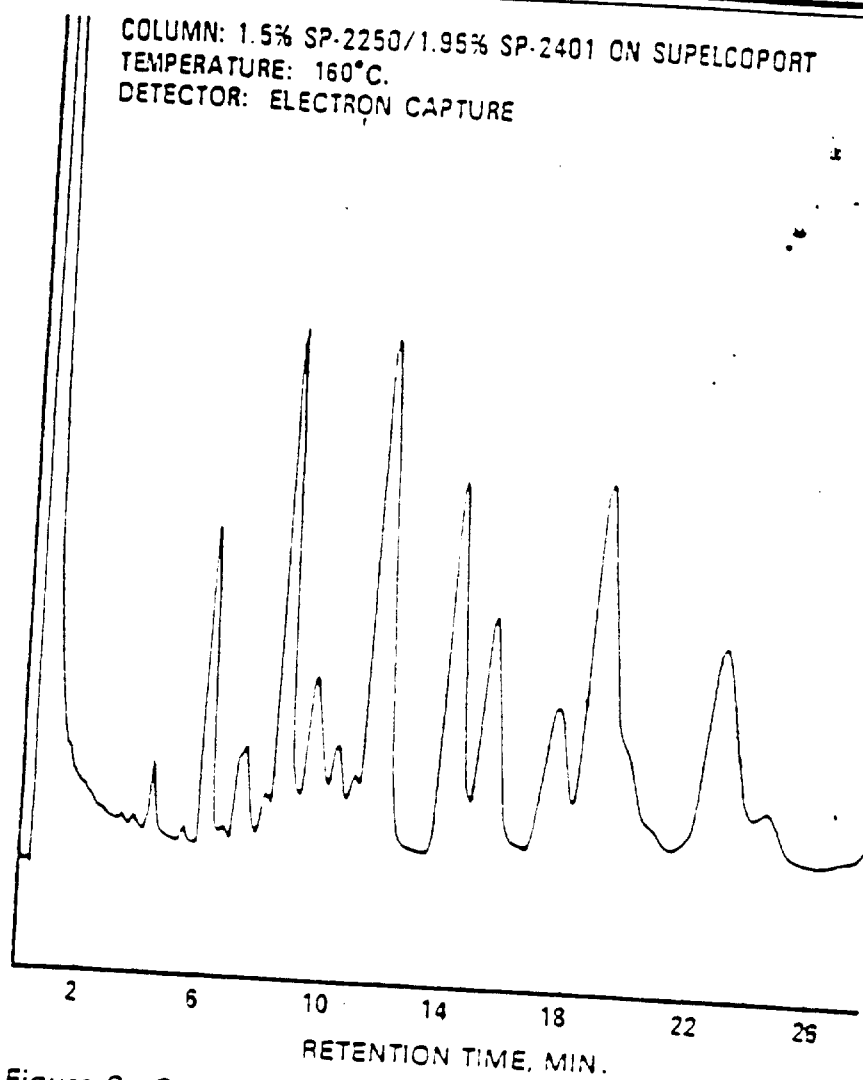


Figure 8. Gas chromatogram of PCB-1248.

COLUMN: 1.5% SP-2250/1.95% SP-2401 ON SUPELCOPORT
TEMPERATURE: 200°C.
DETECTOR: ELECTRON CAPTURE

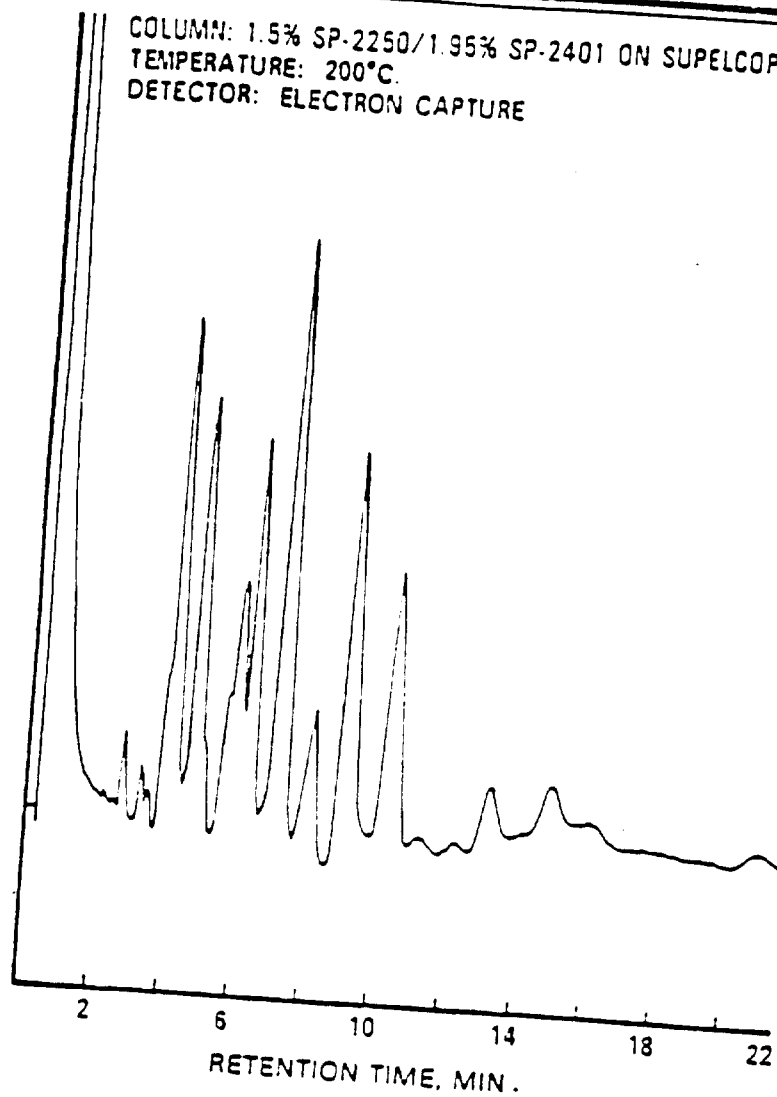


Figure 9. Gas chromatogram of PCB-1254.

COLUMN: 1.5% SP-2250/1.95% SP-2401 ON SUPELCOPORT
TEMPERATURE: 200°C.
DETECTOR: ELECTRON CAPTURE

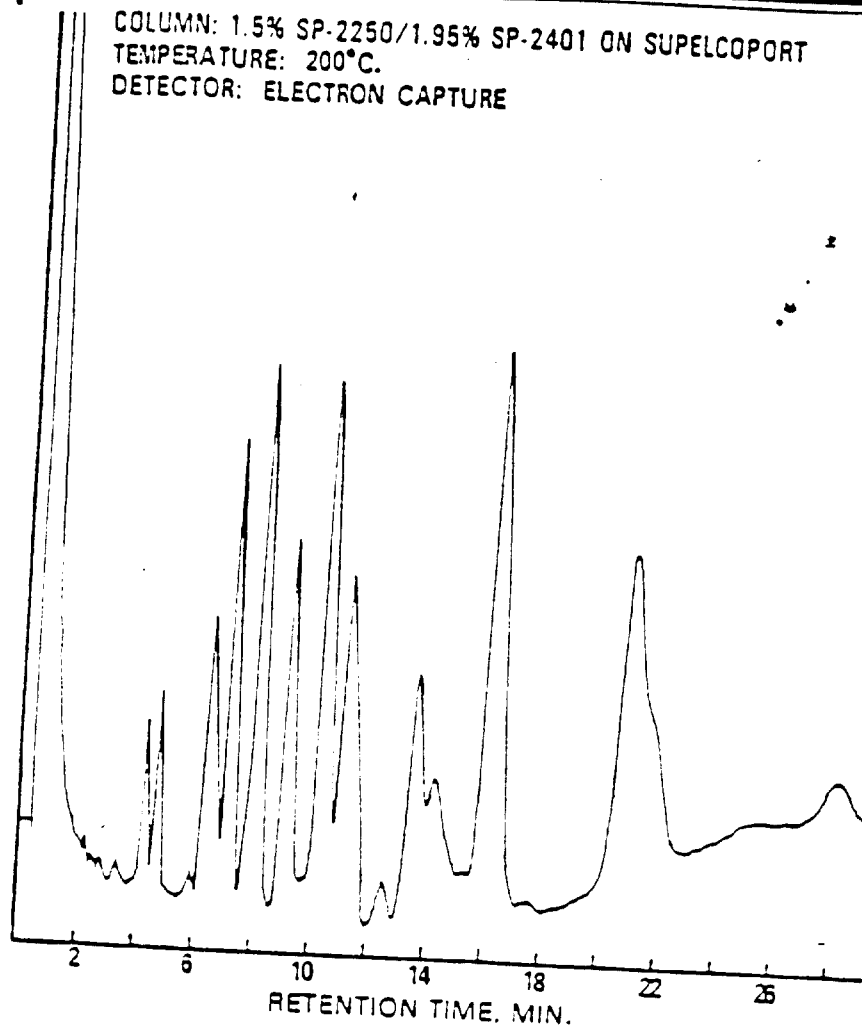


Figure 10. Gas chromatogram of PCB-1260.

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4. USEPA. 1980. Test Methods for Evaluating Solid Waste, Hazardous Waste management system: General, US Environmental Protection Agency, Cincinnati, Ohio. EPA-5-19-80, vol. 45-No. 98, Book 2, p33063-33285.
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NOTE: All the Carbamate Pesticide references are found in the NH QA/QC PP-Section 10.27.

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Data Reduction, Validation and Reporting

If a laboratory is to produce quality data, it is essential that any data produced is adequately reviewed prior to release. New Hampshire is committed to the production of accurate data, and adequate checks to ensure quality data are implemented.

After generation of the data by the instrument, computer or analytical technique, the data is reviewed by the analyst. If a problem has occurred, the analyst reruns the test. Following this, the data is entered into the computer, prior to final report generation. The computer maintains a table of normal values, and if the analyst has entered an abnormal value he is prompted with notification of this fact. If the value is in fact what has been already entered, the analyst makes note of this fact and accepts the entry. On a weekly basis, all samples that have been completed are tabulated. A report is produced from the computer and forwarded to the section head. It is now the section head's responsibility to review all tests run for the sample as far as quality goes and then either approve or reject the data. If the data is approved it is forwarded to the appropriate section heads.

At the same time a parallel but independent check is being performed by the quality assurance officer and advisor. These people review all QC data against known spikes, blanks and duplicates. If a problem shows up in this review, it is the advisor's job to inform both the section head, and the analyst.

Corrective action is implemented by the analyst, section head and quality assurance advisor. If possible, the tests are rerun, if not, the division head is informed of the fact and the sample is retaken.

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In the event that problems persist, the quality assurance officer is informed and it is his job to seek whatever help is required.

Often, the State and the Environmental Protection Agency work together on the same project. In these cases, both the Environmental Protection Agency and State work together to ensure that all data reported is correct.

A number of measurements and observations should be made in the field at the time of sampling. This information is recorded in the field log book with the corresponding sampling number to locate the sampling points on a site plan. These measurements and observations are critical for interpretation of laboratory data. The following list of measurements and observations represent a minimum requirement for surface water samples:

Sample location, relative to fixed points that can be referenced in the future, identification number, date and time.

Water temperature at the point and time of sampling.

Specific conductivity and pH of water sampled - do not immerse indicator paper or electrodes in samples to be sent to the laboratory. Either duplicate samples may be obtained for field measurements or in-situ measurements may be taken if the appropriate equipment or sampling condition is present.

Depth of stream or pond (average and at sample point).

Velocity of stream estimated from object floating on the surface.

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Weather conditions (temperature, cloud cover, recent precipitation or drought).

Observable physical characteristics (odor, color, turbidity, etc.).

The following information should be obtained prior to purging and sampling of the well.

Well Information - Obtain whatever information is available regarding well characteristics. Well depth, screened length, casing material, casing diameter and elevation above ground level. Previous water level and previous pumping rates should be recorded in a field notebook or well sampling data sheet. If possible, well logs should also be obtained.

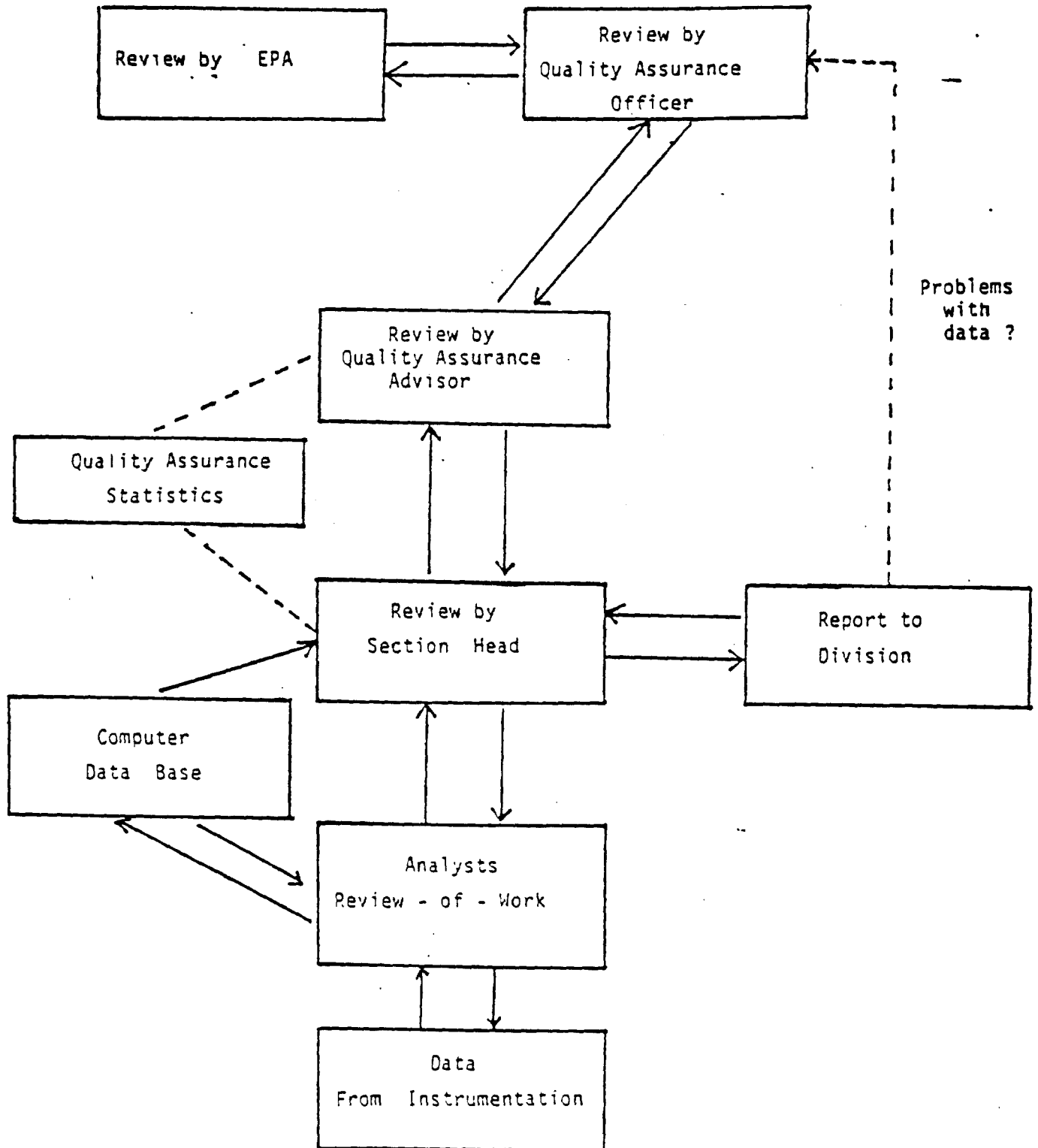
Well Security - Make sure that the well has been locked (with a padlock on a riser pipe, a roadway box, etc.) and note any number, tags or distinguishing marks. Check for any damage of the well casing.

Well Parameters - A water-level measurement must be made the day of sampling using a survey tape with a plunker (weight) or an electronic measuring device. If the well depth is not known, it can be measured with the survey tape and weight. (The length of the weight must be recorded and taken into account). The difference of the two is the height of water in the well.

Well Volume Calculation - A minimum of three well volumes must be evacuated from the well, or the well can be purged dry before recharging and sampling. In either case, the amount of water to be purged should be calculated and recorded. Table 4 can be used to calculate the well volume by multiplying the height of water in the well by the gallon per foot volume for the appropriate casing inner diameter. The purge volume is then three times the well volume.

Procedures for chain-of-custody/sample tracking and data handling are presented in Section No. 7; Sample Custody and Documentation.

As laboratory and field data are generated for inclusion in the final report, the data is assembled by the appropriate field and office personnel as it is received. The data is copied and filed with the originals going to USPEA's Project Manager.



Internal Quality Control Checks

The specific quality control audits used by New Hampshire Department of Environmental Services are outlined in Section 15.0 - "Corrective Action" - page 1. The specific internal audits used and their origination in the analyses include the following.

A. Blanks

(1) Method Blank

A blank solution (DI water or well water which is free of organic contaminants where appropriate) of the same volume as the samples is treated as a sample for the parameter being measured, including all pretreatment, preparation, holding times, extraction and actual analysis.

Frequency: See individual procedures in Section 10. (1 through 6)

(2) Trip Blanks

Trip blanks will be provided by the contractor.

B. Duplicates

A duplicate sample is taken in the field from the same source, at roughly the same time and treated exactly alike during preparation, transport, extraction and analysis.

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Frequency: 1 per sample batch or 20% - Refer to the SOP for the parameter of interest - section 9 of the NH QA/QC PP - for more specific information on duplicates.

C. Spikes

(1) Matrix Spikes

Standards of known amounts are added to a sample. The sample is split - run with and without a spike. The percent recovery of the pure standard spike is taken as a measure of the accuracy of the total analytical method in the sample matrix. It is calculated by the equation:

$$\text{Recovery} = 100X \frac{(\text{final concentration} - \text{original concentration})}{\text{True Value}}$$

assessment of spike recovery and needed reruns will be done before data are reported to the various divisions.

Frequency: 1 per batch (especially for CERCLA & RCRA) - Refer to the SOP for the parameter of interest - section 10 (1 through 46) of the NH QA/QC PP for more specific information.

2) Blind Spike

Submitted by the quality control department on a bimonthly basis - refer to Section 17.0 - 'Corrective Action' - page 1.

D. Accuracy Control Charting

Control charting is no longer done manually by the analyst or the quality assurance department. It is done automatically during the Q.C. Review by the plotting part of the QAD program from the data entered by the analyst after the run. At the end of 3, 6 or 12 months new limits are calculated using the data base generated during that time period. Known QC's duplicates, and spikes are charted using the QAD 10 program with all inorganic parameters, except for those parameters where not enough data is generated during the year. The upper and lower control limits shown on the chart are used as a criteria for action as described in section 10 and section 15 of this manual Section 15 'Corrective Action' discusses in detail significance of these charts in evaluating the status of a particular parameter.

The control limits are derived automatically by the QAD program using these basic calculations:

- a. Standard deviation (Sd) of the difference between the known quantity and the quantity obtained (i.e. spike or standard samples). The calculation for standard deviation is given below.

$$S = \sqrt{\frac{\sum (X - \bar{X})^2}{n-1}}$$

The quantity 's' is based as it is upon a finite number of observations, is only an estimate of the true standard deviation.

The difference $(X - \bar{X})$ is the absolute deviation of the individual result from the experimental mean, the standard deviation is this obtained

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in absolute terms. The degrees of freedom (N-1) is substituted for the number of measurements in the set.

- b. The 95% confidence limits must be determined next. (These are the UWL and the LWL) confidence limit = $s_x t_{95}$

'S' is the standard deviation associated with N measurements.

't' is a factor that depends in magnitude upon the number of measurements as well as the degree of probability for the correctness desired. The values for t are provided in the table given below:

VALUES FOR t FOR VARIOUS LEVELS OF PROBABILITY

Degrees of Freedom	Factor for Confidence Interval (percent)				
	80	90	95	99	99.9
1	3.08	6.31	12.7	63.7	637
2	1.89	2.92	4.30	9.92	31.6
3	1.64	2.35	3.18	5.84	12.9
4	1.53	2.13	2.78	4.60	8.60
5	1.48	2.02	2.57	4.03	6.86
6	1.44	1.94	2.45	3.71	5.96
7	1.42	1.90	2.36	3.50	5.40
8	1.40	1.86	2.31	3.36	5.04
9	1.38	1.83	2.26	3.25	4.78
10	1.37	1.81	2.23	3.17	4.59
11	1.36	1.78	2.18	3.06	4.32
12	1.36	1.78	2.18	3.06	4.32
13	1.35	1.77	2.16	3.01	4.22
14	1.34	1.76	2.14	2.98	4.14
∞	1.29	1.64	1.96	2.58	3.29

- c. The average must also be calculated:

$\bar{x} = \frac{\text{individual values obtained}}{\text{Total \# of Stds.}}$

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- d. The 99% confidence limits - UCL & LCL - is calculated by the following equation:

$$\text{confidence limit} = s_x t_{99}$$

Again the factor for 't' is taken from the table given above.

- e. A Precision Control Chart is developed by collecting data for many samples, a minimum of 15 to 20, run in duplicate under assumed controlled conditions. Once these data have been generated, preferably over an extended period of laboratory time, the following steps should be followed to construct the control chart:

- a. List the range (R) for each set of samples. That is, the absolute value of the difference between each set of duplicate samples. This list can be obtained by listing the QAD 10 entries to a printer.
- b. Calculate the average range (R) by summing the list of R values and dividing by the number of sets of duplicates. The QAD 10 program will calculate the average when the data is listed.

$$R = N$$

- c. Calculate the upper control limit (UCL) on the range according to the formula:

$$UCL_R = D_4 R$$

($D_4 = 3.27$ on all our precision charting, since only duplicates are run.)

Ignore the limit calculated by the QAD 10 program

- d. Calculate the upper warning limit (UWL) on the range according to the formula:

$$UWL_R = 2/3 (D_4 R - R) + R$$

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which for duplicate samples reduces to:

$$UWL_R + 2.51 R = 2.51 R$$

(Ignore the limit calculated by the QAD 10 program

This UWL corresponds to the 95% confidence level.)

An example of NHWSPCC Laboratory's Precision charting has been included in this section.

FACTORS FOR COMPUTING CONTROL CHART LINES

<u>Observations in</u> <u>Subgroup ()</u>	<u>Factor</u> <u>D4</u>
2	3.27
3	2.58
4	2.28
5	2.12
6	2.00
7	1.92
8	1.86

Inherent in the Shewart approach is recognition of the basic assumption that variations exist in every method. That is, no procedure is so perfect, so unaffected by its environment, that it will always give exactly the same assay value or product. Where such situations seem to exist, either the device used to measure the process is not sensitive enough or the person making the measurements is not performing properly. For our purposes, the recorded difference between paired samples should never be less than one-half the minimum detectable limit of the parameter under consideration.

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The organic lab has a quality control logbook, in which the daily response factors are recorded, as well as the percent recovery from the matrix spikes used that day. Also recorded is the relative abundances of the Tuning Spectra, on a daily basis. Examples of these quality control check sheets have been included in this section.

F. Reagents and Standards

All purchased reagents and standards, used at New Hampshire Water Supply and Pollution Control Commission, are certified as to their accuracy by the company of manufacture. All solvents are ACS grade, all standards are certified through the Nation Bureau of Standards or the American Chemical Society.

All acids and bases made at the laboratory are routinely standardized by the quality control department.

For more detailed information, refer to Section 9, Analytical Procedures.

G. Compressed Gases

All compressed gases are purchased through a reputable company, and are guaranteed for purity. Hydrocarbon and moisture traps have been placed on lines from the high purity gases.

H. On the following page is a chart listing the analytes which are commonly done at the New Hampshire WSPCC Laboratory. The quality control given with each listed analyte, was generated as described in this section. The data is

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based on standards spiked into DI water or on duplicate samples. The data base was generated from Jan.1, 1986 to June 27, 1986

H = the number of quality control standards used to develop the QC data.

LDL = All duplicates run over the past year were lower than detectable limits.

CND/pdl

(7780X)

INTERNAL QUALITY CONTROL CHECKS

(DEVELOPED AS DESCRIBED IN SECTION 10 #1 THROUGH 64 QUALITY CONTROL)
(A1) Units are in mg/L, unless otherwise stated).

PARAMETERS		NOMINAL VALUE		X UCL X LCL		UCL-LCL % OF N		N R		3.27 R	
A. INORGANICS											
FLAME METALS											
1. Aluminum	2.0 mg/L	10	2.10	3.09-1.11	55.6-154.4	7	.12	0.39			
2. Barium	2.0 mg/L	23	1.97	2.24-1.70	85-112	INSUFFICIENT DATA					
3. Calcium	3.0 mg/L	15	3.01	3.61-2.41	80.3-120.4	8	.30	0.98			
4. Copper	0.3 mg/L	23	.2997	.308-.292	97.2-102.6	8	.0125	0.041			
5. Iron	0.7 mg/L	82	.7018	.845-.559	79.8-120.7	82	.0293	0.096			
6. Magnesium	0.7 mg/L	INSUFFICIENT DATA									
7. Manganese	0.1 mg/L	81	.1048	.127-.083	82.8-126.8	81	.0072	.0024			
8. Nickel	0.2 mg/L	22	.2088	.265-.152	76.2-132.6	INSUFFICIENT DATA					
9. Potassium	0.5 mg/L	INSUFFICIENT DATA									
10. Sodium	20 mg/L	80	19.325	21.1-17.6	87.8-105.4	80	.553	1.81			
11. Zinc	0.10 mg/L	17	.1049	.127-.083	83.2-126.6	12	.03	.098			
FURNACE METALS											
1. Aluminum	0.2 mg/L	8	.201	.291-.111	55.5-145.5	INSUFFICIENT DATA					
2. Antimony	.02 mg/L	INSUFFICIENT DATA									
3. Arsenic	.02 mg/L	45	.0185	.0246-.0124	61.9-123.1	17	.0016	.0052			
4. Cadmium	.01 mg/L	18	.0095	.0132-.0058	57.6-132.4	9	.0001	.00033			
5. Chromium	.05 mg/L	18	.0541	.0682-.04	80-136.4	11	.0091	.02976			
6. Lead	0.1 mg/L	27	.1026	.1275-.0777	77.1-127.5	16	.0025	.0082			
7. Molybdenum	.02 mg/L	INSUFFICIENT DATA									
8. Nickel	.02 mg/L	10	.002	LDL-.022	?-109.8	INSUFFICIENT DATA					
9. Selenium	.020 mg/L	19	.0203	.0252-.0154	77.2-125.8	11	.0005	.0016			
10. Silver	0.10 mg/L	16	.0944	.076-.123	76-112.8	15	.008	.026			
11. Vanadium	0.04 mg/L	INSUFFICIENT DATA									
OTHER METALS											
1. Mercury	.002 mg/L	15	.002	.0023-.0017	85.3-114.7	8	LDL	N/A			

INTERNAL QUALITY CONTROL CHECKS

(DEVELOPED AS DESCRIBED IN SECTION 10 #1 THROUGH 64 QUALITY CONTROL)
(All units are in mg/L, unless otherwise stated).

PARAMETERS	NOMINAL VALUE	N	\bar{X}	\bar{X} UCL \bar{X} LCL	UCL-LCL % OF N	N	\bar{R}	3.27 \bar{R}
NON METALS								
1. Alkalinity	10 mg/L	68	10.1	11.2-9.0	89.7-112.3	45	.063	.21
2. Ammonia	1.40mg/L	21	1.41	1.55-1.27	91-110.4	15	.083	.27
3. Chlorides	35.4 mg/L	94	36.0	40.3-31.7	89.6-113.7	41	.29	.95
	71 mg/L	80	71.6	76.3-66.9	94.3-107.4	41	.29	.95
	3.54 mg/L	66	4.1	5.5-2.7	75.9-155.7	41	.29	.95
4. Flourides	.38 mg/L	112	.376	.431-.321	84.5-113.4	71	.008	.03
	.95 mg/L	105	.949	1.04-.863	90.8-109	71	.008	.03
	1.52 mg/L	105	1.535	1.64-1.43	94-108	71	.008	.03
	1.9 mg/L	111	1.921	2.02-1.82	95.9-106.3	71	.008	.03
5. Hardness	40 mg/L	188	39.98	42.1-37.8	94.6-105.3	149	.027	.09
6. Nitrates	0.7 mg/L	93	.72	.78-.67	95-110.7	43	.031	.10
	1.4 mg/L	80	1.43	1.53-1.33	94.7-109.6	43	.031	.10
	0.14 mg/L	67	.145	.179-.111	79.3-127.9	43	.031	.10
7. pH	7.0	219	7.01	7.05-6.97	99.6-100.7	170	.033	.11
8. T. Phosphorus	.050 mg/L	16	.053	.066-.040	79.7-132.3	24	.002	.007
	.250 mg/L	17	.251	.266-.236	94.5-106.3	24	.002	.007
9. Spec. Cond.	147 u MHOS	63	146.1	159.1-133.1	90.5-108.3	38	3.14	10.3
10. Sulfates	9.6 mg/L	27	9.7	11.2-8.2	85.6-116.5	23	.37	1.21
11. TKN	2.5(AL)mg/L							
	1.75 mg/L	10	1.71	1.96-1.46	83.2-112.2	12	.07	.23
	2.50 mg/L	10	2.58	3.26-1.90	76.1-130.3	12	.07	.23
	3.50 mg/L	10	3.50	3.96-3.0	87-113	12	.07	.23
12. Turbidity	1.8 NTU							
	18 NTU	14	18.4	20.6-16.2	90-114			

INSUFFICIENT DATA

INSUFFICIENT DATA

PARAMETERS	NOMINAL VALUE
------------	------------------

1. BOD	4.8 ALPHA
2. COD	34.3 ALPHA
3. TOC	14.1 ALPHA

1. Oil & Grease

2. MBAS

3. T. Residue

4. T. Non-Filt

Residue

B. RADIOLOGY

1. Gross Alpha

2. Radium

3. Radon Gas

4. Uranium

00 (0112)

Performance and System Audits

A. Blind Performance Audits

A blind audit is submitted to the laboratory by the quality assurance department on a bi-monthly basis. The audit is given a "false" location name and submitted by a sampler or other means, insuring that laboratory workers are unaware that an audit is taking place. The data collected from these tests are maintained by the QA department in a confidential notebook. Data falling outside of the 99% confidence interval, as calculated by following the procedures detailed in section 13.0 pp 4&5, is immediately dealt with by contacting the section supervisor and having all data for that run reviewed, and rerun, if necessary. If all other QC for that run is correct, release of the reports is at the discretion of the supervisor. If this is not the case, the entire run is repeated.

Data falling outside of the 95% confidence range is flagged by analyst and test. Records are maintained on repeat problems by the same analyst or on the same test. This data (between 95% and 99% confidence) is used to locate problem tests and/or the need for additional training of laboratory personnel.

B. Capability Check

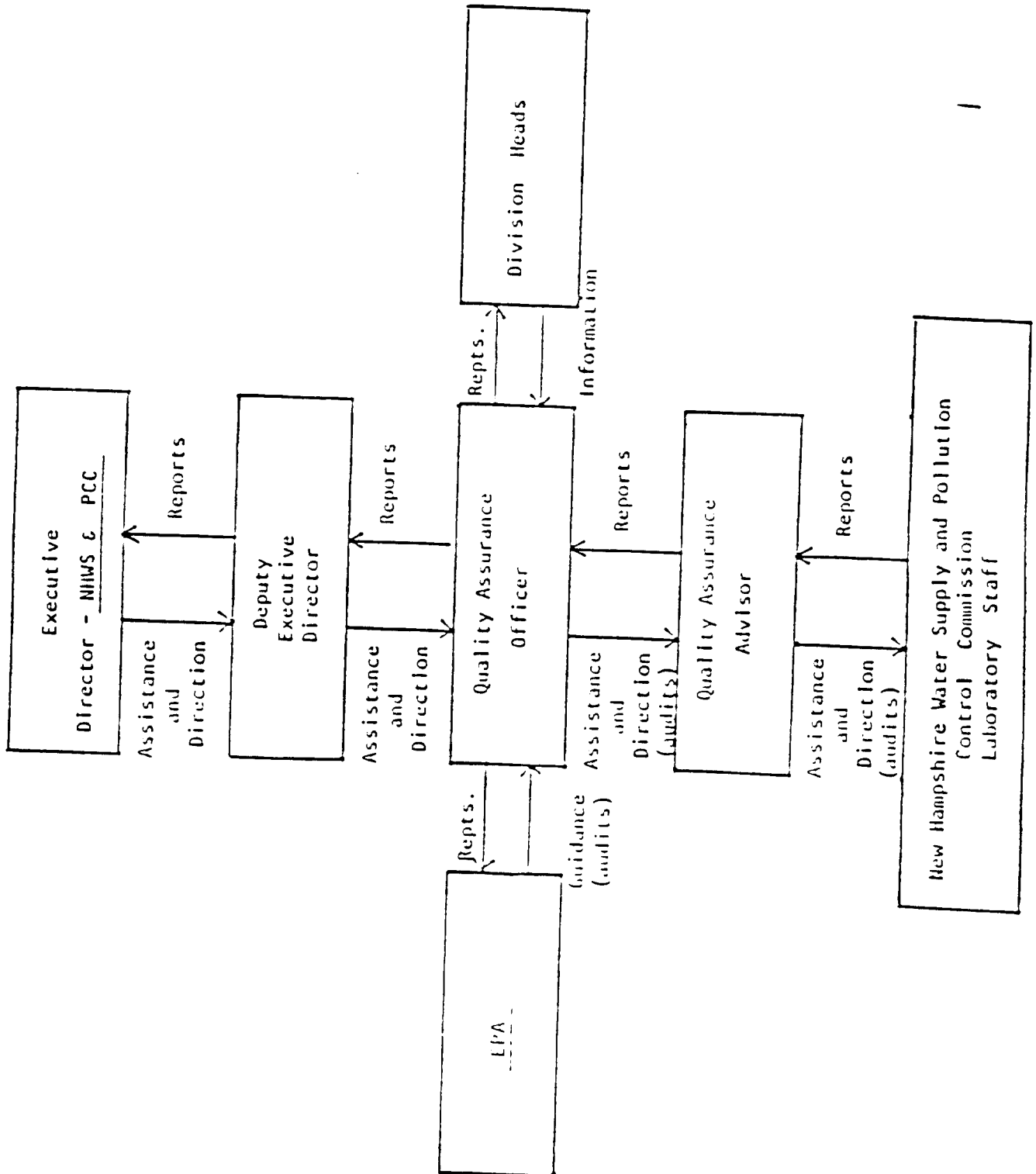
Before any priority pollutant analyses are done by the New Hampshire Water Supply and Pollution Control Commission laboratory, a set of samples are sent to the laboratory by the Environmental Protection Agency. Performance on these samples must be satisfactory in order for the laboratory to receive real samples. Bi-yearly performance evaluation samples are then sent to re-verify the lab capability, these are the above-mentioned Water Supply Study and the Water Pollution Study.

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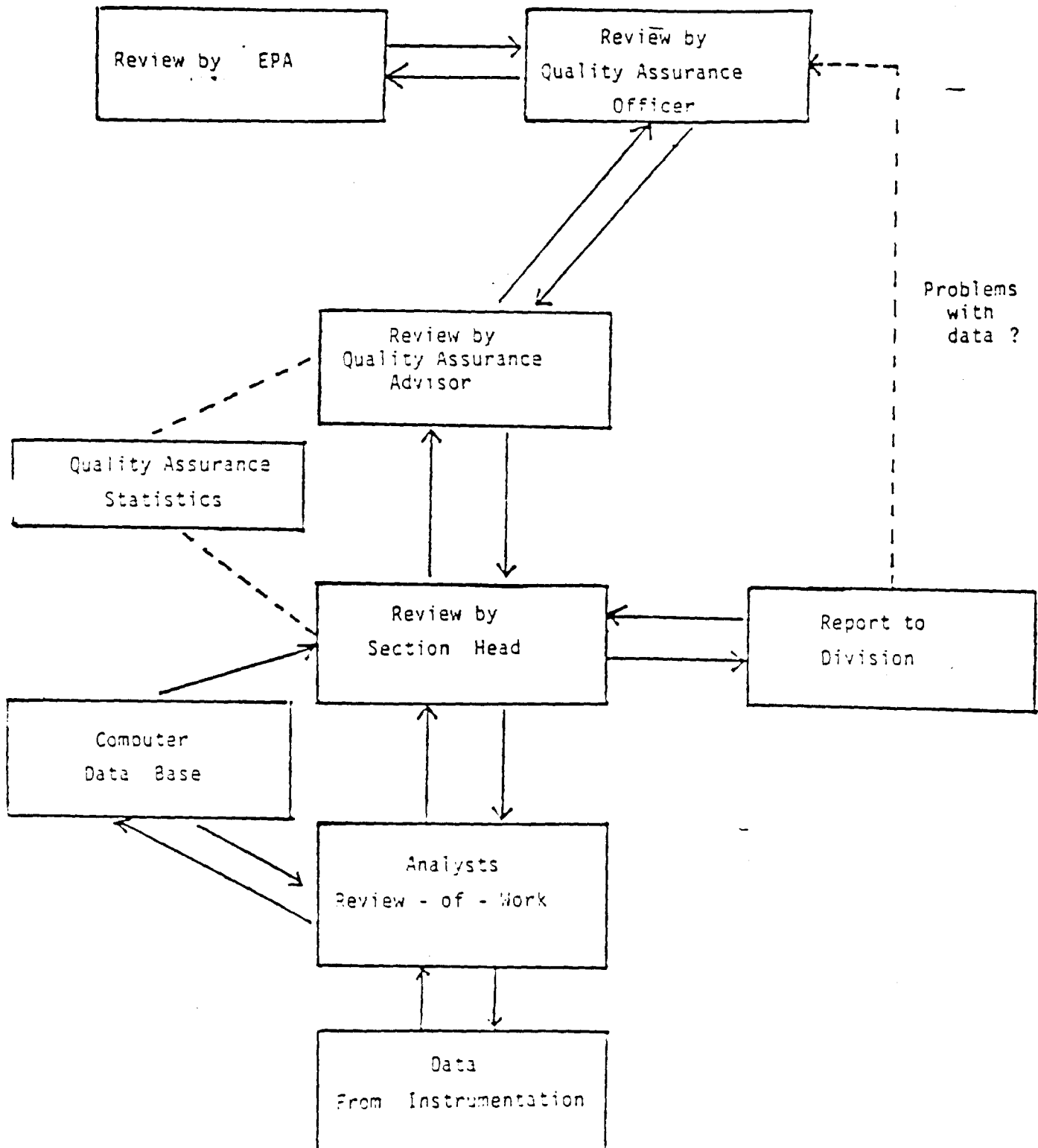


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LIST OF INSTRUMENTS, MANUALS TO GO WITH THE INSTRUMENTS,
AND LOCATION OF MANUALS

- A. Gas Chromatograph/Mass Spectrometer
 - 1. Manuals
 - a. 5985 Users Manuals Volumes 1-5 05985-90027
to 05985-90030
 - b. 5985 GC/MS System Options (1) 05985-90093
 - c. 5985 GC/MS System Quick Start Manual
 - d. 5985 GC/MS System Maintenance and Installation Manuals
24396-14001
to 24396-14004
 - 2. Location
 - a. Organics Lab manual storage bookshelves
- B. Infrared Spectrophotometer Model 281-283
 - 1. Manuals
 - a. Users Manual
 - 2. Location
 - a. Pesticides "Wet" Lab in drawer under instrument
- C. Perkin Elmer Sigma 1B Gas Chromatograph
 - 1. Manuals
 - a. Sigma Console Users Manual
 - b. Sigma Programming Manual
 - c. BASIC II Language Instructions
 - 2. Location
 - a. Organics Lab manual storage bookshelves
- D. Hewlett Packard 5880A Gas Chromatograph
 - 1. Manuals
 - a. Gas Chromatograph Instrument manual
 - b. Operator Training manual
 - c. Site Preparation manual
 - 2. Location
 - a. Organics Laboratory manual storage bookshelves
- E. Hewlett Packard 5700A Gas Chromatograph
 - 1. Manuals
 - a. Gas Capillary Inlet System
 - b. Operating Manual
 - c. Service Manual
 - 2. Location
 - a. Organics Laboratory manual storage bookshelves

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LIST OF INSTRUMENTS, MANUALS TO GO WITH THE INSTRUMENTS,
AND LOCATION OF MANUALS

- F. Varian Aerograph 2400 Gas Chromatograph Manuals
 - 1. Manuals
 - a. ⁶³Ni Electron Capture Instruction Manual
 - b. Alkali Flame Detector Instruction Manual
 - 2. Location
 - a. Organics Laboratory manual storage bookshelves
- G. Teckman Purge/Trap and Auto Sampler manuals
 - 1. Manuals
 - a. White manuals for Mass Spec Purge Trap
 - b. Orange Manuals-for 5880A GC
 - 2. Location
 - a. Organics Laboratory Manual storage bookshelves
- H. Photovac 10A10 Operating Manual
 - 1. Location
 - a. Organics Laboratory manual storage bookshelves
- I. Furnace and Flame Atomic Absorption manuals
 - 1. Manuals
 - a. Analytical Methods for Atomic Absorption Spectrophotometry, Perkin Elmer
 - b. Clinical Methods for Atomic Absorption Spectrophotometry, Perkin Elmer
 - c. Analytical Methods Using HGA Graphite Furnace
 - d. Model 560 Atomic Absorption Spectrophotometry
 - e. Analytical Methods for Furnace Atomic Absorption Spectrophotometry 4/14/81
 - f. Analytical Methods for Atomic Absorption Spectrophotometry 6/24/77
 - g. Perkin Elmer HGA Graphite Furnace Operator's Manual
 - h. Perkin Elmer AS-40 Auto Sampler Operator's Manual
 - 2. Location
 - a. Water Laboratory office area
- J. Hewlett Packard 1084-B liquid chromatograph manuals
 - 1. Manuals
 - a. Operating manual
 - b. Operating manual short form
 - c. Training Documentation
 - 2. Location
 - a. "Wet Chemistry" portion of the Organics Laboratory

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LIST OF INSTRUMENTS, MANUALS TO GO WITH THE INSTRUMENTS,
AND LOCATION OF MANUALS

- K. Analytical Balance manuals
 - a. CAHN TA-450 Users manual
 - 2. Location
 - a. "Wet Chemistry" portion of the Organics Laboratory
- L. Technician Auto Analyzer II System
 - 1. Manuals
 - a. Auto Sampler IV Instruction manual
 - b. Proportioning Pump II Instruction manual
 - c. Colorimeter II Instruction manual
 - d. Electrochemical Detector II Instruction manual
 - e. Two Pen Recorder Instruction manual
 - 2. Location
 - a. Lab Office - in John Pepin's Desk
- M. Hack Model 18900 Ratio Turbidimeter
 - 1. Manuals
 - a. Instruction Manual
 - 2. Location
 - a. Drawer below turbidimeter in the Inorganics Lab
- N. Orion Ammonia Electrode Model 95-10
 - 1. Manuals
 - a. Instruction manual
 - 2. Location
 - a. Drawer below ammonia meter in the Inorganics Lab
- O. Orion Specific Ion Meter Model 407A/L
 - 1. Manuals
 - a. Instruction Manual
 - 2. Location
 - a. Drawer below fluoride meter in the Inorganics Lab
- P. Bausch & Lomb Spectronic 710 Spectrophotometer
 - 1. Manuals
 - a. Operator's Manual
 - 2. Location
 - a. Drawer below spectrophotometer in the Inorganics Lab

LIST OF INSTRUMENTS, MANUALS TO GO WITH THE INSTRUMENTS,
AND LOCATION OF MANUALS

- Q. 4959 Electrolytic Conductivity Bridge
1. Manuals
 - a. Operating manual
 - b. General instructions for YSI 3400 Series Conductivity Cells
 2. Location
 - a. Drawer below the conductivity bridge in the Inorganics Lab
- R. Beckman Model 915 Total Organic Carbon Analyzer and 191840 Air Purification Unit
1. Manuals
 - a. Instruction manual
 2. Location
 - a. Drawer below the analyzer in Inorganics Lab
- S. Beckman Model 215 B Infrared Analyzer
1. Manuals
 - a. Instruction Manual
 2. Location
 - a. Drawer below the analyzer in the Inorganics Lab
- T. YSI 5700 Series Dissolved Oxygen Probe
1. Manuals
 - a. Instruction manual
 2. Location
 - a. Drawer below the probe in the Inorganics Lab
- U. Perkin Elmer Coleman 50 Mercury Analyzer System
1. Manuals
 - a. Instruction Manual
 2. Location
 - a. Bookshelf in the Inorganics Lab
- V. Albrecht Walk-in Cooler
1. Manuals
 - a. Instruction manual
 2. Location
 - a. Files in Quality Assurance Office

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LIST OF INSTRUMENTS, MANUALS TO GO WITH THE INSTRUMENTS,
AND LOCATION OF MANUALS

- W. Beckman LS-100 Liquid Scintillation System and Direct Data Readout Module
 - 1. Manuals
 - a. Instruction Manual
 - 2. Location
 - a. Radiology Office
- X. Ludlum Model 2200 Scaler Rate Meter
 - 1. Manuals
 - a. Instruction manual
 - 2. Location
 - a. Radiology Office
- Y. Ludlum Model 1000 Six Decade Scaler
 - 1. Manuals
 - a. Instruction manual
 - 2. Location
 - a. Radiology Office
- Z. Carter Model 2-5C Scintillation Detector
 - 1. Manuals
 - a. Operating and Maintenance Procedures
 - 2. Location
 - a. Radiology Office
- AA Nuclear-Chicago Model 192A Netrascaler
 - 1. Manuals
 - a. Operation and Maintenance manual
 - 2. Location
 - a. Radiology Lab
- BB National Incubators (Heinicke) - Model 3512
 - 1. Manuals
 - a. Operator's Manual
 - 2. Location
 - a. Microbiology file cabinet marked "Lab Manuals"

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LIST OF INSTRUMENTS, MANUALS TO GO WITH THE INSTRUMENTS,
AND LOCATION OF MANUALS

- CC Series 10 Microstar Microscope (A0)
1. Manuals
 - a. Operator's Manual
 2. Location
 - a. Microbiology file cabinet marked "Lab Manuals"
- DD Castle 3122 autoclaves
1. Manuals
 - a. Operator's Manual
 2. Location
 - a. Microbiology file cabinet marked "Lab Manuals"
- EE Kold-Draft Ice Machine
1. Manuals
 - a. Operator's Manual
 2. Location
 - a. Microbiology file cabinet marked "Lab Manuals"
- FF Hotpack Incubator
1. Manuals
 - a. Operator's Manual
 2. Location
 - a. Microbiology file cabinet marked "Lab Manuals"
- GG Hydrosol Stainless 47 mm Filter Holders
1. Manuals
 - a. Operator's Manual
 2. Location
 - a. Microbiology file cabinet marked "Lab Manuals"
- HH Heinicke HN-1 + 2 Washers - 2
1. Manuals
 - a. Operator's Manual
 2. Location
 - a. Microbiology file cabinet marked "Lab Manuals"

LIST OF INSTRUMENTS, MANUALS TO GO WITH THE INSTRUMENTS,
AND LOCATION OF MANUALS

- II New Brunswick Sterilizer & Dispensor
 - 1. Manuals
 - a. Operators manual
 - 2. Location
 - a. Microbiology file cabinet marked "Lab Manuals"
- JJ Baird Atomic Fluorimet
 - 1. Manuals
 - a. Operators manual
 - 2. Location
 - a. Microbiology file cabinet marked "Lab Manuals"
- KK Blue M Water Bath
 - 1. Manuals
 - a. Operators manual
 - 2. Location
 - a. Microbiology file cabinet marked "Lab Manuals"
- LL Labconco Laminar Flow Cabinet
 - 1. Manuals
 - a. Operators manual
 - 2. Location
 - a. Microbiology file cabinet marked "Lab Manuals"
- MM Beckman DU-7 Spectrophotometer
 - 1. Manuals
 - a. DU-7 Spectrophotometer Operating Manual
 - b. Dot Matrix Printer Operation Manual
 - 2. Location
 - a. Drawer below instrument
- NN Dionex Series 4000i Ion Chromatograph
 - 1. Manual
 - a. Operating Manual
 - 2. Location
 - a. Drawer below instrument

14.0 Specific Routine Procedures Used to Assess Data Precision, Accuracy, and Completeness

A. Organics

(1) Qualitative and Quantitative Criteria

Since there are many interferences with the determination of volatile organics, base/neutrals, phenols, and low level pesticides, it is of the utmost importance that positive identification be made. Samples for these particular parameters are initially screened by GC, but always run on GC/MS for positive I.D.

The initial screen allows the analyst to properly dilute the sample for GC/MS analysis.

(2) Tuning Spectra Criteria

Daily monitoring of the Tuning Spectra is done. Examples of the necessary ion abundance criteria to be met are included in this write-up.

B. Inorganics

(1) Qualitative and Quantitative Criteria

The individual analytical procedures describe the necessary standards, quality control checks, and standard curves needed to accurately qualitate and quantitate for a particular parameter.

The accuracy charting establishes confidence limits for each particular parameter, and it is the responsibility of the analyst to be aware of these confidence limits.

C. Central Tendency and Dispersion

(1) Arithmetic Mean (\bar{X})

Calculated for each parameter tested by the New Hampshire Water Supply and Pollution Control Commission, by using at least 10 data points. Every accuracy quality control chart, defines the arithmetic mean obtained for that particular quality control standard.

definition:

$$\bar{X} = \frac{\text{the sum of the data points}}{\text{the number of data points involved}}$$

(2) Standard Deviation(s)

Calculated for each parameter tested by the New Hampshire Water Supply and Pollution Control Commission, by using at least 10 data points. Every accuracy quality control chart indicates the 2s and 3s around the mean.

definition:

$$S = \sqrt{\frac{\sum (X - \bar{X})^2}{n-1}}$$

(3) Measures of Variability

A % Bias (%B) - the difference between the average value (\bar{X}) of a set of measurement of a standard T given by:

$$\%B = 100 (\bar{X} - T) / T$$

A reference standard was analysed at least ten times before the % Bias was calculated.

D. Precision

Involves the closeness of data values to each other. It was calculated for each parameter by determining the sample coefficient of variation:

$$CV = 100 S / \bar{X}$$

To obtain an arithmetic mean and standard deviation a reference standard was analyzed at least ten times before the calculations for a mean and standard deviation was performed.

E. Accuracy

Involves closeness of measurements to a reference. Value and incorporates both bias and precision. The calculation for the percent bias of each parameter, represents this laboratory's accuracy for that particular parameter.

F. Completeness

All samples received by the laboratory are analysed, therefore 100% completeness is obtained in every parameter.

G. Minimal Detection Limit (99% confidence)

(1) Calculation:

$$MDL = S_m (t_{.99})$$

Where:

S_m = The standard deviation of the responses, in concentration units.

$t_{.99}$ = "Student's t value" appropriate for a one tailed test at 99% confidence level and a standard deviation estimate with $m-1$ degrees of freedom.

(2) Procedure

(a) The MDL was determined in reagent water (blank), prepared as a laboratory standard (analyte in reagent water) at a concentration which is at least equal to or in the same concentration range as the estimated MDL. (Between 1 and 5 times the estimated MDL). This procedure was used to determine the MDL's if analytes are detected on such instruments as the Atomic Absorption Units, the Gas Chromatographs and the GC/MS.

(b) The concentration value that corresponds to three times the standard deviation of replicate instrumental measurements for the analyte in reagent water. This procedure was used to determine all other MDLS which are given.

(c) A minimum of ten aliquots of the sample were processed through the entire analytical method. All computations were made according to the defined method with final results in the method reporting units. If blank measurements were required to calculate the measured level of the analyte, separate blank measurements were obtained for each sample aliquot analyzed. The average blank measurement was subtracted from the respective sample measurements.

(3) Reporting

Section 10.0 of the NH QA/QC PP identifies the required analytical method to be employed for each specific analyte. In addition the MDL, % Bias, and % Precision is given for that particular analyte, analyzed by the cited method. The MDL for each analyte is expressed in

the appropriate method reporting units.

As stated in the introduction to Section 10.0, as the historical data develops for each individual project site, the MDL will be established for the sample matrix of that site.

A. Calculations for the GC/MS Quality Control Duplicate Worksheet:

$$\% \text{ Recovery} = \frac{\text{Amount Detected}}{\text{True Value}} \times 100$$

(Note: This formula for calculating % Recovery is only used for standards spiked into organic free water or D1 water where appropriate. For matrix spikes use formula described on Page 2 of this section.)

B. Calculations for the GC/MS Quality Control Calibration Check Worksheet:

$$\% \text{ Difference} = \frac{\overline{RF} - RF}{RF} \times 100$$

RF = Response Factor give the day standard was run.

\overline{RF} = Response Factor from the previous run of that standard.

STATE OF N.H. WATER POLLUTION CONTROL LABORATORY

CORRECTIVE ACTION:

A. Responsibilities:

1. The laboratory technicians must report to the unit supervisor and/or the quality assurance advisor, when quality control limits (UCL_x/LCL_x) exceeded or a definite trend appears to be developing.
2. The responsibility of the unit supervisor:
 - a. To ensure the technician was following the laboratory's standard operating procedure.
 - b. To ascertain the status of the instrument and see that repairs are conducted correctly.
3. The responsibility of the quality assurance advisor:
 - a. To ensure all standards are accurate and within the hold time.
 - b. To review all quality control data at least once a week.
 - c. To ensure data is not to be generated on any system that is flagged as out-of-control, until corrective action has been taken and has been shown to solve the problem.
 - d. To submit blind spikes to ensure a test is operating correctly, and the problem has been solved.
 - e. To inform the quality assurance officer on a weekly basis as to the lab status.
4. Corrective action is documented by the form attached. A form for each parameter is filled out, on a weekly basis, by the QC advisor and reviewed by the Unit Supervisor and QC Officer. In addition, a short memo is prepared summarizing the status of Quality Control in both laboratory sections for the week.

B. Independent External Audits:

The Water Supply and Pollution Control Commission participates in biannual audits given by EPA. These audits test both water supply parameters and water pollution parameters. Once an analytical problem has been identified by EPA, an investigation into the problem is initiated by both the QC officer and the laboratory unit supervisor. Corrective action is taken to solve the problem, and a written explanation of both the problem and the corrective response is given to the Region I EPA QC coordinator, by the WSPCC QA officer.

C. Internal Audits

The QC advisor submits to the laboratory, with the cooperation of the field samplers, blind spike samples on a bimonthly basis. These spikes are submitted as actual samples, which allows the quality control department to monitor the actual processing of samples and data.

Test: pH
Unit Supervisor: _____
QC Officer: _____

QC Inspector: _____
Date Inspected: _____
Date Received: _____
Date Received: _____

Part I STANDARD AND REAGENTS

Standards	Reagents	Date Made/ Rec'd	Hold Limit	Comparison to the previous
	7.00 Buffer (QC Std)		Indef.	
	10.00 Buffer (Calb. Std)		Indef.	
	4.00 Buffer (Calb. Std)		Indef.	

Part II

ACCURACY CONTROL CHART (X)

- Is the QC Std. being run once every 20 samples? _____
a) If not how often is the QC Std. run? _____
b) Which technician(s) is performing less than the required number of Std.? _____
- Is the accuracy control charting current? _____
a) If not what was the date of the last sample plotted? _____
b) What was the date of the last sample run? _____
c) Who is the technician(s) responsible for the testing? _____
d) What sample numbers are involved? _____
- Are there any points in the Upper Control Limit (UCL \bar{x}) area of the chart? _____
a) Who is the technician responsible for the testing? _____
b) How many data points are involved? _____
c) What sample numbers are involved? _____
d) What was the date of the testing? _____
- Are there any points in the Upper Warning Limit (UWL \bar{x}) area of the chart? _____
a) Who is the technician responsible for the testing? _____
b) How many data points are involved? _____
c) What sample numbers are involved? _____
d) What was the date of the testing involved? _____
- Are there any data points in the Lower Control Limit (LCL \bar{x}) area of the chart? _____
a) If so, who is the technician responsible for the testing? _____
b) How many data points are involved? _____
c) What sample numbers are involved? _____

6. Are there any data points in the Lower Warning Limit (LWLx) area of chart? _____

- a) If so, who is the technician(s) responsible for the testing? _____
- b) How many data points are involved? _____
- c) What sample number(s) are involved? _____
- d) What was the date of the testing involved? _____

7. Are there any TRENDS developing on the chart? _____

- a) How many data points are involved in the trend? _____
- b) What range of time does the trend span? _____
- c) Is the trend high or low? _____

Part III PRECISION - Duplicates

1. Are duplicate samples being run, one per sample group? _____

- a) If not, who is the technician(s) responsible for the testing? _____
- b) How frequently are duplicates being performed? _____
- c) Are duplicates within 10% of each other? _____

Part IV CORRECTIVE ACTION TAKEN BY THE QC DEPARTMENT

Signature _____ Date _____

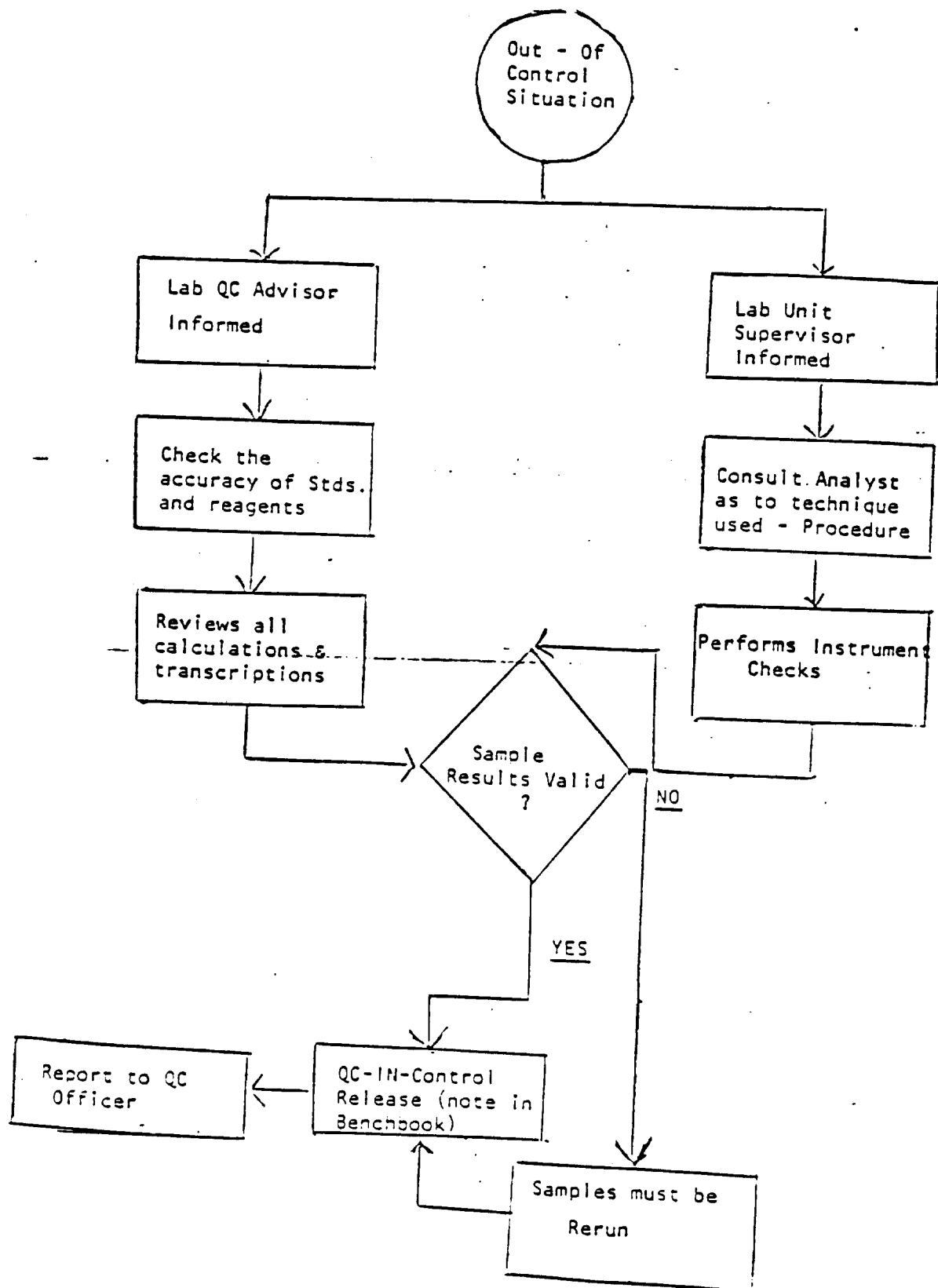
Part V CORRECTIVE ACTION TAKEN BY THE UNIT SUPERVISOR

Signature _____ Date _____

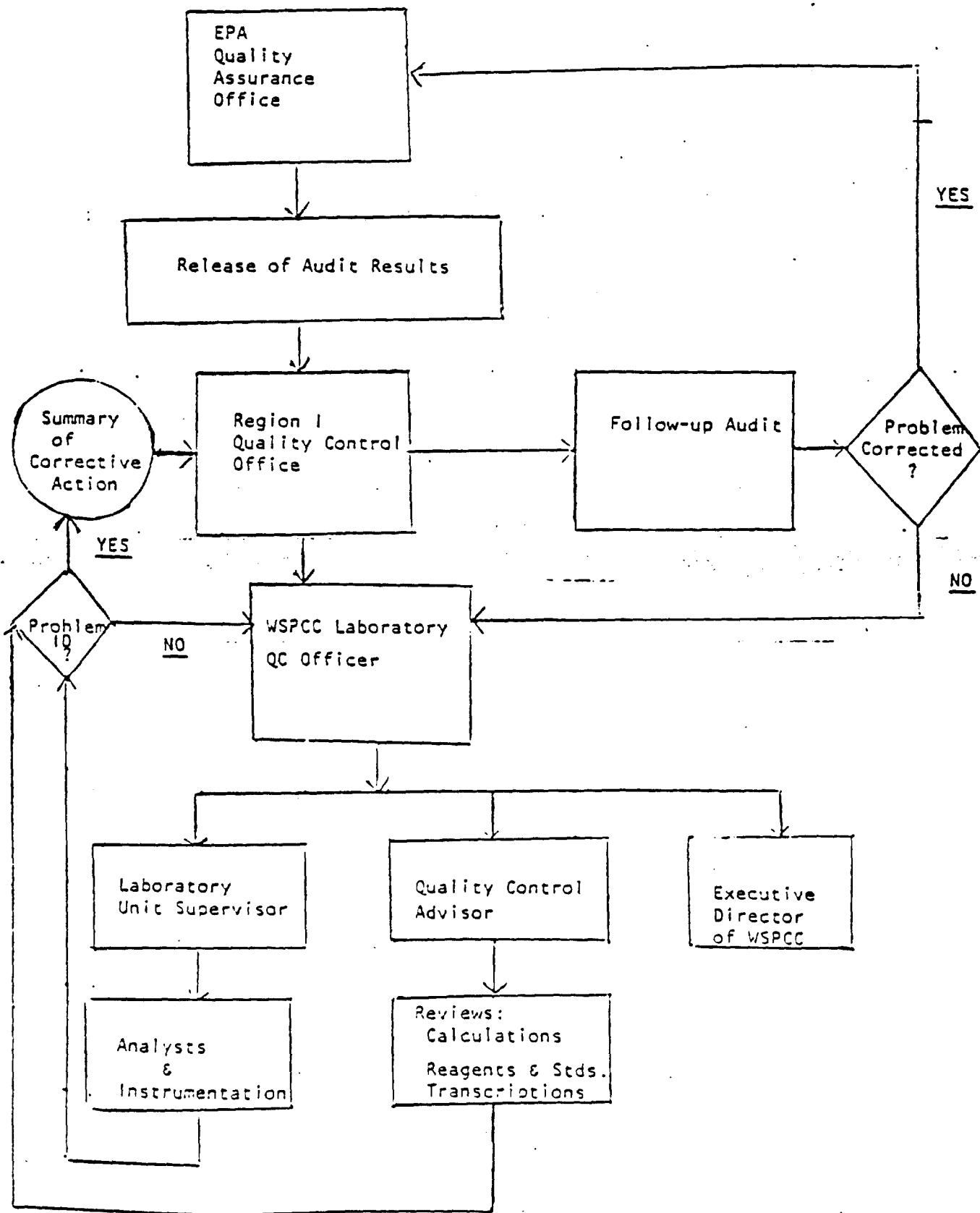
Part VI RELEASE OF DATA

- 1. Were the samples rerun? _____
- 2. Was sample data released? When? _____

DAILY OPERATIONS OF LAB CORRECTIVE ACTION FLOW



RESPONSE OF LAB TO EPA WS AND WP AUDITS



Quality Assurance Reports
to Management

Section No: 16.0
Revision No: 1
Date : 11/28/84
Page : 1 of 2

For the quality assurance program to work, there must be sufficient review by management at all levels. This is needed because if problems occur management must be fully aware so that sufficient priority can be placed on those areas that would remedy the problem. New Hampshire has such a program.

Laboratory workers report difficulties and problems to the laboratory quality assurance advisor. It is this person's responsibility to investigate the difficulties with the worker in an attempt to solve them. The quality assurance advisor reports bi-weekly to the quality assurance officer about any problems that have occurred, and about how they were solved. This report is by written memo.

These reports are reviewed by the quality assurance officer and feedback is provided to the quality assurance advisor and laboratory workers. The interaction between quality assurance officer, quality assurance advisor and lab workers is on an as-needed basis except for the scheduled review of all routine charts, spikes, duplicates and blind unknowns, which is performed on a weekly basis.

It is the quality assurance officer's responsibility to report to the division heads about specific problems involving data affecting that division. This occurs whenever review of the data indicates that there may be a problem. It is also the quality assurance officer's job to provide the Environmental Protection Agency with information about the lab performance on the Environmental Protection Agency spikes and Environmental Protection Agency system audits.

